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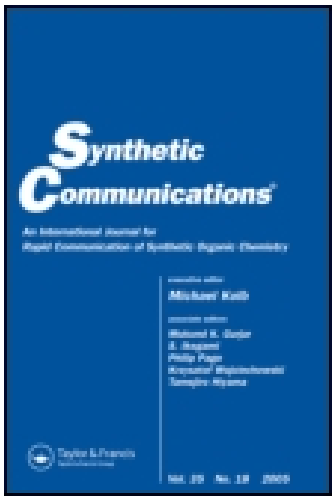

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RING OPENING OF EPOXIDES WITH CARBOXYLATES AND PHENOXIDES IN MICELLAR MEDIA CATALYZED WITH $Ce(OTf)_4$

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RING OPENING OF EPOXIDES WITH CARBOXYLATES AND PHENOXIDES IN MICELLAR MEDIA CATALYZED WITH $Ce(OTf)_4$

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ABSTRACT

Efficient ring opening reaction of epoxides with carboxylates and phenoxide anions catalyzed with ceric triflate is performed in micellar media. This new method is a useful procedure for the preparation of β-carboxy and phenoxy alcohols from epoxides under mild reaction conditions.

It is well established that micelles as media for chemical reactions, present interesting features which are influenced by the micellar environmental factors.[1] These factors can result changes in the reaction rate, mechanism, regio, and stereochemistry, and the scope of the reaction.[2–6] Despite the extensive studies on the analytical applications and catalytic activity of micelles,[7–11] the occurrence of organic reactions and especially

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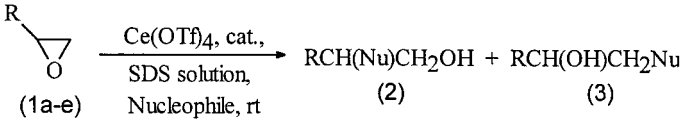
Lewis acid catalysis in micellar media are rarely studied.[12] Most classical Lewis acids used are unstable in aqueous media and are hydrolyzed easily and therefore, study on the catalytic activity of stable Lewis acids in aqueous and micellar media is a useful investigation.

The ring opening reaction of epoxides by nucleophiles is an interesting approach in organic synthesis.[13] This reaction with nucleophiles such as CN^-,[14–16] N_3^-,[17] NO_3^-,[18] and halides[19] have been performed in both organic and aqueous organic solvents. The reactions of epoxides with carboxylic acids are generally limited to the reaction of acetic acid catalyzed with different Lewis acids.[18b,20a] The use of NaOAc/HOAc[20c] and benzoic acid/Co(salen)/*i*-Pr_2NH[20d] are also reported.

Ring opening reaction of epoxides with phenols has also been performed, but the reaction usually occurs in the presence of tertiary amines or under alkaline conditions at 80–130°C.[21] We now wish to report an efficient method for the ring opening of epoxides with carboxylates and phenoxide anions in micellar media at room temperature using ceric triflate [$Ce(OTf)_4$], as the catalyst (Scheme).



(1a-e) (2) (3)

Epoxide = (a): Cyclohexene oxide, R = (b): Ph, (c): $PhOCH_2$,
(d): CH_2=$CHCH_2O$, (e): $HOCH_2$,
Nu: PhONa, 4-ClC_6H_4ONa, 4-$CH_3OC_6H_4ONa$, CH_3CO_2Na,
$CH_3CH_2CO_2Na$, $C_6H_5CO_2Na$

Scheme.

When we performed the reaction of styrene oxide with sodium acetate in water or in aqueous acetonitrile and in the presence of 0.1 molar equivalents of $Ce(OTf)_4$, a very slow reaction occurred in both cases (Table 1, Entries 1, 2). Therefore, in order to increase the rate of reaction, the effect of different micellar media on the progress of the reaction was examined. We first studied the effect of cetyltrimethylammonium bromide (CTAB) as a cathionic, sodium dodecyl sulfate (SDS) as an anionic and triton X-100 as a neutral micelle on the ring opening reaction of styrene oxide with sodium acetate. The results obtained for these reactions are shown in Table 1.

Results of Table 1 show that in the absence of either micelle (Table 1, Entries 1, 2) or the catalyst (Table 1, Entry 5), the reaction of styrene oxide

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Table 1. Effects of Different Micelles[I] for the Conversion of Styrene Oxide to 2-Phenyl-2-acetoxy-1-ethanol with Sodium Acetate Catalyzed with 0.1 Molar Equivalents of $Ce(OTf)_4$ at Room Temperature

Entry	Reaction Media	Time (h)	Yield %[II]
1	Water[III]	10	8
2	20% aq. CH_3CN[III]	7	15
3	SDS (8.1×10^{-2} M)	0.5	87
4	SDS (8.1×10^{-3} M)	3	80
5	SDS (8.1×10^{-2} M)[IV]	3	25
6	CTAB (1.3×10^{-3} M)	7	43
7	CTAB (1.3×10^{-2} M)	3	60[V]
8	CTAB (8.1×10^{-3} M)	0.5	65[V]
9	Triton X-100 (3.0×10^{-4} M)	7	40
10	Triton X-100 (6.0×10^{-4} M)	7	55

[I]The CMC of SDS $= 8.1 \times 10^{-3}$ M,[11b] CTAB $= 1.3 \times 10^{-3}$ M,[11b] Triton X $= 3.0 \times 10^{-4}$ M (2%).[11c]
[II]Isolated yield.
[III]The reaction was performed in the absence of micelle.
[IV]The reaction was performed in the absence of $Ce(OTf)_4$.
[V]The formation of β-bromohydrine (15–35%) was also occurred in this micellar solution.

with sodium acetate is very slow. However, the rate of reaction is increased in micellar media at critical micelle concentration (CMC) or above it. In SDS micellar solution, the reaction was completed after 30 min and 87% of the corresponding product was obtained (Table 1, Entry 3). In micellar solution of cetyltrimethylammonium bromide either at or above the critical micelle concentration, (Table 1, Entries 6, 7), the reaction of styrene oxide was found to be some how slower than in SDS solution and was not completed. However, when the reaction was performed in the same concentration as SDS solution (Table 1, Entry 8), the reaction was completed after 30 min but, the formation of β-bromohydrine which occurs through the reaction of bromide ion with epoxide, increases as the concentration of the micellar solution is increased. Similarly, the solution of triton X-100 both at and above its critical micelle concentration, (Table 1, Entries 8, 9), was found not to be a suitable micellar media, since the reactions were not completed after several hours.

Due to the cheapness and more clean reaction of styrene oxide in SDS micellar solution, we choose SDS solution (~ 0.1 M) as a suitable reaction media for the ring opening of epoxides with different carboxylates. The reaction of epoxides carrying electron-releasing or withdrawing groups with

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sodium acetate and propionate occurred efficiently at room temperature and their corresponding β-carboxy alkanols were obtained in high yields. It was interesting to apply this method for ring opening of epoxides with a less reactive carboxylate such as sodium benzoate. When sodium benzoate was reacted with styrene oxide under the same reaction conditions as applied for sodium acetate, the reaction furnished the corresponding 2-phenyl-2-benzoxy-1-ethanol in 84% yield after 30 min (Table 2, Entry 7). However, this reaction in the absence of micelle did not proceed at all and styrene oxide was remained intact. The results obtained for the reaction of epoxides with carboxylates are shown in Table 2.

Due to the importance of the reaction of epoxides with phenols from biological points of view,[21c] and in order to avoid the strong alkaline conditions for this important synthetic transformation, we decided to apply our method for the ring opening of epoxides with phenoxide anions. We first studied the reaction of different substituted epoxides with

Table 2. Reaction of Epoxides with Carboxylates and Phenoxides Catalyzed with $Ce(OTf)_4$ in SDS (0.1M) at Room Temperature

Entry	Epoxide	Nuclephile	Mole Ratio of Sub./Cat./ NaNu	Product	Time (h)	Yield[I] (%)	Reference to the Product.
1	1a	CH_3CO_2Na	1/0.1/1.5	–[II]	2	85	18b, 20
2	1b	CH_3CO_2Na	1/0.1/1.5	2b	0.5	87	18b, 20
3	1c	CH_3CO_2Na	1/0.1/1.5	3c	1	85	18b, 20
4	1d	CH_3CO_2Na	1/0.1/1.5	3d	1	88	18b, 20
5	1a	$C_2H_5CO_2Na$	1/0.1/1.5	–[III]	4	80	22, 23
6	1b	$C_2H_5CO_2Na$	1/0.1/1.5	2b	5	88	24, 23
7	1c	$C_2H_5CO_2Na$	1/0.1/1.5	3c	5	83	23
8	1a	$PhCO_2Na$	1/0.1/1.5	–[IV]	1	90	20e
9	1b	$PhCO_2Na$	1/0.1/1.5	2b	0.5	84	25
10	1d	$PhCO_2Na$	1/0.1/1.5	3d	2	87	25
11	1a	PhONa	1/0.1/1.5	–[V]	3	92	26
12	1b	PhONa	1/0.1/1.5	2b	3	90	27
13	1c	PhONa	1/0.1/1.5	3c	1	85	28
14	1e	$4\text{-}ClC_6H_4ONa$	1/0.1/1.5	3e	4	89	21c
15	1e	$4\text{-}MeOC_6H_4ONa$	1/0.1/1.5	3e	1	91	21c

[I]Isolated Yield.
[II]2-Hydroxycyclohexyl acetate.
[III]2-Hydroxycyclohexyl propionate.
[IV]2-Hydroxycyclohexyl benzoate.
[V]2-Hydroxycyclohexyl phenyl ether.

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sodium phenoxide in 0.1 molar solution of SDS and in the presence of 0.1 molar equivalents of $Ce(OTf)_4$ as catalyst. The reactions occurred at room temperature and the corresponding β-phenoxy alkanols were obtained in high yields (Table 2). The reaction was then successfully performed with electron-withdrawing substituted phenols such as 4-chloro, and 4-methoxy phenols (Table 2, Entries 13, 14).

In conclusion, using a combination of micellar media and $Ce(OTf)_4$ as an stable Lewis acid in aqueous media provides a new, efficient and simple method for ring opening of epoxides with both aliphatic and aromatic carboxylates and also with electron-donating and -withdrawing substituted phenoxide anions at room temperature. The possibility of using carboxylates instead of their carboxylic acids at room temperature, and the absence of strong alkaline conditions for ring opening of epoxides with phenol are the strong practical points of this method.

EXPERIMENTAL

Products were characterised by comparison of their physical data with those of known samples. All yields refer to isolated products. IR spectra were recorded on Perkin Elmer 781 spectrometers. NMR spectra were recorded on Bruker DPX 250.

Catalytic Ring Openig of Styrene Oxide with Sodium Benzoate in the Presence of $Ce(OTf)_4$ in SDS Solution as Typical Procedure

A solution of cyclohexene oxide (98 mg, 1 mmol) in SDS (0.1 M, 3 mL) was prepared. Sodium benzoate (217 mg, 1.5 mmol) and ceric triflate (73.6 mg, 0.1 mmol) were added to this solution. The reaction mixture was stirred at room temperature for 1 h. The mixture was extracted with $CHCl_3$ (4×10 mL) and solid NaCl was added during the extraction to remove the emulsion. The organic layer was dried with anhydrous Na_2SO_4. The solvent was evaporated and the resulting mixture was applied on a short column of silica gel. Elution with petroleum ether gave 2-hydroxycyclohexyl benzoate in 90% yield, m.p. 104–106°C, Lit.[20d] 105.5–107.5°C.

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25. The products were isolated and identified by their spectral data. $PhCH(OCOPh)CH_2OH$, IR (neat), ν (cm^{-1}): 3450, 3075, 3040, 2990, 2880, 2830, 1725, 1605, 1455, 1320, 1270, 1115, 980, 790, 755, 710, 700, ^{1}H-NMR ($CDCl_3$), δ (ppm): 7.2–7.7 (10H, m), 6.0 (1H, t), 3.8 (2H, d), 3.4 (1H, s), ^{13}C-NMR ($CDCl_3$), δ (ppm): 174.2, 141.4, 139.7, 130.2, 129.4, 129.0, 128.5, 127.5, 125.1, 71.8, 69.3; $CH_2{=}CHCH_2OCH_2CH(OH)CH_2OCOPh$: IR (neat), ν (cm^{-1}): 3360, 3100, 3060, 3020, 2980, 2875, 1720, 1645, 785, 700; ^{1}H-NMR ($CDCl_3$), δ (ppm): 7.2–7.7 (5H, m), 5.8 (1H, complex), 5.0 (2H, complex), 3.85 (2H, d), 3.2–3.5 (5H, complex), ^{13}C-NMR ($CDCl_3$), δ (ppm): 168.2, 141.4, 129.4, 128.5, 127.5, 125.4, 120.3, 72.8, 65.3, 58.9, 45.5.
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