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# CERIC AMMONIUM NITRATE, AN EFFICIENT CATALYST FOR MILD AND SELECTIVE OPENING OF EPOXIDES IN THE PRESENCE OF WATER THIOLS AND ACETIC ACID

N. Iranpoor*, I. Mohammadpour Baltork, F. Shiriny Zardaloo
Department of Chemistry, Shiraz University
Shiraz, Iran

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Abstract: *Ring opening of epoxides with catalytic amounts of Ce(IV) as ceric ammonium nitrate (CAN) are performed efficiently in the presence of water, Thiols and acetic acid under mild conditions. The epoxides are opened with high regio-and stereoselectivity and with good to excellent yields. The products formed from the reaction of polar substituted epoxides in acetic acid were found to be derivative of succinic acid diester. The mechanism of the reaction is believed to be a radical type, involving the formation of an epoxonium radical cation.*

## INTRODUCTION

Ring opening of epoxides in the presence of different uncleophiles, under mild and neutral conditions is important in modern organic synthesis[1]. However, standard methods for nucleophilic opening of epoxides are often far from ideal and usually encounter some disadvantages such as: high acidity[2,3], unsatisfactory regioselectivity[3], inconvienent handling of the reagent[4,5] and long reaction time[4].

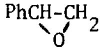
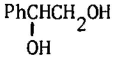
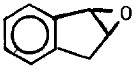
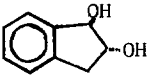
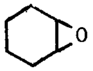
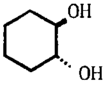
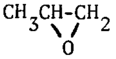
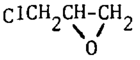
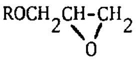
Recently we have reported the use of 2,3-dichloro-5,6-dicyano-p-benzoquinone and ceric ammonium nitrate[6,7,8] as one-electron transfer catalysts for ring opening of epoxides and thiiranes in alcohols.

In this paper, we have investigated the possibility of using Ce(IV) as an efficient catalyst for regio-and stereoselective ring opening of epoxides in the presence of water. thiols and acetic acid under mild and neutral conditions.

## RESULTS AND DISCUSSION

Ring opening reactions of different classes of epoxides such as cyclohexene and cyclopentene oxides, styrene and indene oxides, epichlorohydrine and Allyl-2,3-epoxy propyl ether as examples of alicyclic, aryl and polar substituted epoxides with Ce(IV) as CAN in the presence of water were performed at room temperature and in good yields. The corresponding diols were separated and compared with authentic samples. The results are tabulated in Table 1.

Table 1. Reaction of epoxides with Ce(IV) as CAN in water and in mixture of water: acetonitrile (1:3) at room temperature.

| Epoxide | mole% CAN | Time[a] (min) | yield[a] | Time[b] (min) | yield[b] | Product |
|---|---|---|---|---|---|---|
|  $\underset{\diagdown O \diagup}{PhCH{-}CH_2}$ | 0.2 | 10 | 85 | 25 | 80 |  $\underset{OH}{PhCH}CH_2OH$ |
|  | 0.2 | 20 | 70 | 30 | 62 |  |
|  | 0.4 | 100 | 82 | 160 | 75 |  |
|  $\underset{\diagdown O \diagup}{CH_3CH{-}CH_2}$ | 0.4 | 100 | 70 | 160 | 62 | $CH_3CHOHCH_2OH$ |
|  $\underset{\diagdown O \diagup}{ClCH_2CH{-}CH_2}$ | 0.6 | 120 | 80 | 180 | 64 | $ClCH_2CHOHCH_2OH$ |
|  $\underset{\diagdown O \diagup}{ROCH_2CH{-}CH_2}$ | 0.6 | 120 | 70 | 180 | 62 | $ROCH_2CHOHCH_2OH$ |

R- $CH_2{=}CH{-}CH_2$

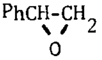
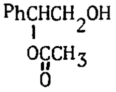
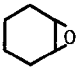
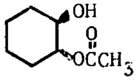
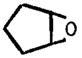
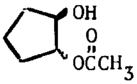
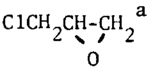
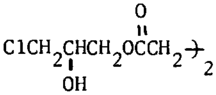
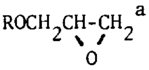
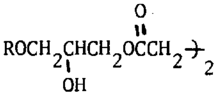
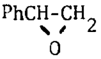
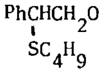
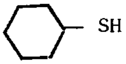
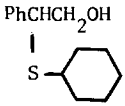
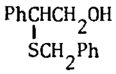
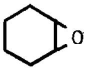
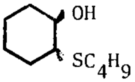
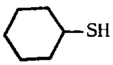
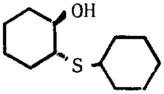
a- reaction was performed in water.

b- reaction was performed in mixture of water-acetonitrile(1:3).

Reactions of styrene oxide, cyclohexene and cyclopentene oxides in acetic acid with catalytic amountes of Ce(IV) were occured very fast and at room temperature. The reactions were also examined under reflux conditions. The products obtained under both conditions were found to to be 2-acetoxy-2-Phenyl ethanol, trans-2-acetoxy cyclohexanol and trans-2-acetoxy cyclopentanol respectively. However, reactions of polar substituted epoxides, such as epichlorohydrine and allyl-2,3-epoxypropyl ether were performed only under reflux conditions. Bis(3-chloro-2-hydroxy-propyl) and bis(1-allyloxy-2-hydroxypropyl) succinate were obtained respectively in high yields and were identified both by their spectral data and also by their hydrolysis to the succinic acid. The results are shown in Table 2.

Ring opening reaction of epoxides with different thiols catalyzed by Ce(IV) was performed in refluxing acetonitrile. The corresponding β-hydroxy sulfides were obtained in good yields. The results are tabulated in Table 2.

Table 2. Reaction of acetic acid and thiols with epoxides in the presence of Ce(IV).

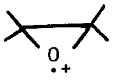
| Epoxide | Nucleophile | mole% of CAN | Time (min) | yield | Product |
|---|---|---|---|---|---|
|  $PhCH\underset{O}{-}CH_2$ | $CH_3CO_2H$ | 0.2 | 5 | 80 |  $PhCH(OCOCH_3)CH_2OH$ |
|  | " | 0.3 | 10 | 82 |  |
|  | " | 0.3 | 15 | 75 |  |
|  $ClCH_2CH\underset{O}{-}CH_2$ [a] | " | 0.4 | 20 | 79 |  $(ClCH_2CH(OH)CH_2OCOCH_2 )_2$ |
|  $ROCH_2CH\underset{O}{-}CH_2$ [a] | " | 0.6 | 30 | 80 |  $(ROCH_2CH(OH)CH_2OCOCH_2 )_2$ |
|  $PhCH\underset{O}{-}CH_2$ | $n\text{-}C_4H_9SH$ | 0.2 | 5 | 60 |  $PhCH(SC_4H_9)CH_2OH$ |
| " |  | 0.2 | 90 | 60 |  |
| " | $PhCH_2SH$ | 0.2 | 90 | 70 |  $PhCH(SCH_2Ph)CH_2OH$ |
|  | $n\text{-}C_4H_9SH$ | 0.4 | 30 | 69 |  |
| " |  | 0.4 | 180 | 75 |  |

R: $CH_2$=CH-$CH_2$

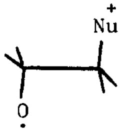
a: the reaction was performed under reflux condition.

Although the precise mechanism of the reaction is not clear, but on the basis of the results obtained from the reaction of epoxides with nucleophiles catalyzed by Ce(IV) and in the presence of acrylamide as a radical traping agent[9], the assumption of radical cations (I) and (II) as intermediates may account for the above features of the reaction.

Catalytic nature of the reaction could be due to the regeneration of Ce(IV) from the reaction of radical cation (II) and Ce(III).



(I)



(II)

Nu= $H_2O$, $CH_3CO_2H$, RSH

In addition, the formation of bis(3-chloro-2-hydroxy propyl) and bis(1-allyloxy-2-hydroxy propyl) succinate from the reactions of epichlorohydrine and allyl-2,3-epoxy propyl ether with acetic acid could be a good evidence for the occurance of a radical type reaction.

## EXPERIMENTAL

Products were characterized by comparison with authentic samples or with their spectral data. The reactions were monitored by thin layer or gas chromatography. All yields refer to the isolated products.

General Procedure for the Reaction of Epoxides in Water: A mixture of epoxide (10 mmole) and water (100 ml) was treated with (0.1-0.8) molar equivalents of CAN at room temperature for 5-120 min. (Table 1). The progress of the reaction was monitored by t.l.c. using $CCl_4/CH_3OH$ (40/3) as eluent. The reaction mixture was saturated with sodium chloride and the product was extracted with ether several times or with continuous extraction. The etherate was dried ($MgSO_4$) and evaporated. Column chromatography on silica-gel using n-hexane: $CCl_4$(1:1) as eluent or recrystalization from ethyl acetate gave the diol in 65-90% yield (Table 1). The products were compared with authentic samples. Melting points and spectral data of the products are show below.

a) Phenyl-1,2-ethanediol: m.p 66-68°(Lit[10], m.p, 65-67°C); $\nu_{max}$(KBr): 3260(s), 3060(s), 3055(w), 2967(s), 2935(s), 2870(w), 1605(m), 1495(s), 1450(s), 1110(s), 1025(s), 750(s), $cm^{-1}$. N.m.r ($CDCl_3$) $\delta$ (ppm): 7.3(5H, singlet), 4.7(1H, doublets of doublet), 3.67(2H, singlet), 3.5(2H, doublet of doublets).

b) trans-1,2-Indanediol: m.p. 159-160°C (Lit[11].m.p, 160-163). N.m.r(DMSO); $\delta$ (ppm) 7.15(4H, complex), 5.15(1H, doublet), 5.02(1H, doublet), 4.02(1H, multiplet), 3.05(1H, quartet), 2.27(1H, quartet).

c) trans-1,2-cyclohexanediol; m.p 102-104°C(Lit[12],m.p 105°C); $\nu_{max}$(KBr), 3360(s), 2930(s), 2860(s), 1450(s), 1070(s), 995(s) $cm^{-1}$; N.m.r ($CDCl_3$), $\delta$ (ppm) 4.0-4.7 (2H, singlet), 3.0-3.6 (2H, multiplet), 1-2.1 (8H, complex).

d) 3-chloro-1,2-propanediol : $n_D^{20}$, 1.4791 (Lit[13] $n_D^{20}$, 1.4809; $\nu_{max}$(neat) 3450(s), 2955(s), 2930(s), 2890(s), 1433(s), 1100(s), 1035(s) $cm^{-1}$; N.m.r ($CDCl_3$) $\delta$ (ppm) 4.15-3.45(5H, complex), 3.05-2.55(2H, singlet).

e) 3-allyloxy-1,2-propanediol: $n_D^{20}$, 1.4592; $\nu_{max}$(neat); 3380(s), 3085(w), 3015(w),2970(s), 2930(s), 2870(s), 1555(w), 1455(m), 1423(m), 1100(s), 1050(s), 930(s), 795(w), $cm^{-1}$. N.m.r ($CCl_4$); $\delta$ (ppm) 6.2-5.5 (1H, complex), 5.85-5.4(2H, complex), 4.50-4.0(2H, singlet), 4.0-3.8

(2H, donblet), 3.70-3.0(5H, complex) ppm.

General Procedure for the Reaction of Epoxides in Acetic Acid: A solution of epoxide (5 mmole) in acetic acid (20 ml) was treated with (0.2-0.6) molar equivalent of CAN and stirred at room temperature or under refluxing condition for 5-30 min. (Table 2). The solvent was evaporated. The mixture was also coevaporated with carbon tetrachloride. Water (30 ml) was added and the product was extracted with ether several times. The etherate was washed with a 5% solution of sodium bicarbonate and dried. Evaporation of the solvent followed by vaccum distillation or column chromatography on silica-gel using n-hexane-$CCl_4$(1:1) as eluent gave the corresponding products in 75-82% yield. The spectral data of the product are as below:

a) 2-acetoxy-2-Phenylethanol, $n_D^{25}$ 1.5114, $\nu_{max}$(neat); 3420(s), 3060(w), 3035(m), 2930(s), 2880(s), 2830(s), 1740(s), 1605(m), 1495(m), 1450(s), 1355(s), 1250(s), 1110(s), 1060(s), 755(s), 700(s) $cm^{-1}$ .N.m.r($CCl_4$); $\delta$ (ppm) 7.2(5H, singlet), 5.8(1H, triplet), 5.5(1H, singlet), 3.7(2H, doublet), 2.0(3H, singlet).

b) trans-2-acetoxycyclohexanol[4] and trans-2-acetoxycyclopentanol[14] were identified by comparison with authentic samples.

c) bis(3-allyloxy-2-hydroxypropyl) succinate: $n_D^{25}$=1.4593; $\nu_{max}$(neat); 3420(s), 2960(s), 2880(m), 1740(s), 1650(m), 1440(m), 1380(s), 1260(s), 1100(s), 1000(m), 860(s) $cm^{-1}$; N.m.r ($CCl_4$); $\delta$ (ppm) 6.3-5.6(2H, complex), 5.5-5.1(8H, unresolved multiplet), 4.7-3.9(8H, complex), 3.8-3.4(4H, complex), 2.0(4H, singlet). This product was also hydrolyzed to succinic acid.

d) bis(3-chloro-2-hydroxypropyl) succinate: $n_D^{25}$ 1.4636; $\nu_{max}$(neat); 3400(s), 2980(s), 2920(s), 1730(s), 1440(s), 1380(s), 1250(s), 1100(s), 900(m), 750(s) $cm^{-1}$. N.m.r($CCl_4$); $\delta$ (ppm) 4.55(4H, doublet), 4.3-3.8(2H, complex), 3.6(4H, doublet), 2.1(4H, singlet). This Product was also hydrolyzed to succinic acid.

General Procedure for the Reaction of Epoxides with Thiols: A solution of epoxide (1 mmole) and thiol (1 mmole) in acetonitrile (5 ml) was treated with (0.2-0.4) molar-equivalent of CAN and refluxed for 5-180 min(Table 2). The progress of the reaction was monitored by t.l.c., using $CCl_4$ as eluent. The solvent was evaporated and the residue was washed with ether. The crude product was vaccum distilled or column chromatographed on silica-gel using n-hexane-$CCl_4$ (1:1) as eluent. The corresponding hydroxy sulfides were obtained in 60-70% yield. The spectral data of the products are shown below:

a) 1-(1-Phenyl-2-hydroxy) ethyl-n-butylsulfide: $n_D^{20}$ , 1.5458, $\nu$(neat): 3370(s), 3065(m), 3035(m), 2960(s), 2930(s), 2880(s), 1590(w), 1495(s), 1457(s), 1275(s), 1050(s), 760(s), 700(s) $cm^{-1}$ ; N.m.r ($CCl_4$), $\delta$ (ppm): 7.2(5H, singlet), 5.7(1H, triplet), 3.6(2H, doublet), 3.2(1H, singlet), 2.45(2H, triplet), 1.8-1.0(4H, multiplet), 0.9(3H, triplet).

b) 1-(1-Phenyl-2-hydroxy) ethyl-cyclohexyl sulfide: $n_D^{20}$ , 1.5488, $\nu$(neat), 3380(s), 3070(m), 2935(s), 2858(s), 1580(w), 1498(s), 1455(s), 1260(s), 1050(s), 760(s), 700(s)$cm^{-1}$. N.m.r($CCl_4$), 7.2(5H, singlet), 5.75(1H, triplet), 3.7(2H, doublet), 2.5(1H, singlet), 2.2-1.0(11H, complex).

c) 1-(1-Phenyl-2-hydroxy) ethyl-benzyl sulfide: $n_D^{20}$ 1.5910; $\nu$(neat) 3400(s), 3090(s), 3025(s), 2920(s), 2880(m), 1605(m), 1498(s), 1455(s), 1265(s), 1050(s), 760(s), 700(s) $cm^{-1}$

N.m.r(CCl$_4$), $\delta$ (ppm) 7.2-7.3(10H, two singlets), 5.75(1H, triplet), 3.9-3.3(5H, triplet + two singlets) ppm.

d) trans-(2.hydroxycyclohexyl)-cyclohexyl sulfide: $\nu$(neat) 3400(s), 2935(s), 2855(s), 1450 (s), 1278(s), 1085(s), 998(s), 870(s), 700(m) cm$^{-1}$ .N.m.r.(CCl$_4$); $\delta$ (ppm) 4.8(1H, singlet) 3.8-3,0(2H, complex), 2.9-2.5(1H, multiplet), 2.25-1.3(18H, complex).

e) trans-(2-hydroxycyclohexyl)-n-butyl sulfide: $\nu$(neat) 3400(s), 2960(s), 2940(s), 2860(s), 1455(s), 1375(m), 1080(s), 995(s), 700(m) cm$^{-1}$. N.m.r(CCl$_4$); $\delta$ (ppm) 4.8(1H, singlet), 3.9-3.0 (2H, complex), 3.0-2.5(2H, triplet), 2.5-1.2(12H, complex).

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