Ring opening of α,β-epoxy phenyl ketones with ceric ammonium nitrate (CAN) and potassium bromide

Zhou Lu, Wentao Wu, Lijun Peng, and Longmin Wu

Abstract: Ring-opening reaction of α,β-epoxy phenyl ketones was achieved cooperatively using cerium ammonium nitrate (CAN) and potassium bromide. The reaction occurred regioselectively at the β-C to afford *syn*-β-bromo-α-hydroxyl ketones as main outcomes.

Key words: ring-opening, epoxide, ceric ammonium nitrate, potassium bromide.

Résumé : Utilisant l'effet combiné du nitrate d'ammonium cérique (NAC) et du bromure de potassium comme catalyseurs, on a réalisé la réaction d'ouverture de cycle de α,β-époxy phénylcétones. La réaction se fait d'une façon stéréosélective au niveau du carbone β et elle conduit aux β-bromo-α-hydroxycétones *syn* comme produits principaux.

Mots-clés : ouverture de cycle, époxyde, nitrate d'ammonium cérique, bromure de potassium.

[Traduit par la Rédaction]

Introduction

Epoxides are important starting materials and intermediates in organic synthesis (1) because of their easy preparations and ready reactivities toward nucleophiles. Among the reports on epoxides, many were involved in ring-opening reactions (2). Most of the nucleophilic ring-opening reactions proceeded via an S_N2-like mechanism and afforded the corresponding *trans*-β-Nu alcohols (3). Our recent studies found that nitric oxide (NO) caused ring opening of 2,3-epoxides in either syn- or anti-selective fashion, which is strongly dependent on the α-C substituent (4). It was found that cerium ammonium nitrate (CAN, $(NH_4)_2Ce(NO_3)_6$), a single electron oxidant in organic oxidation reactions (5–11), efficiently catalyzed most ring-opening reactions of epoxides (12). These reactions occurred in distinct regioselectivity, β- or α-attack (12*e*–12*f*), and in anti and (or) syn manners, strongly depending upon the molecular structure, the stoichiometry of CAN used, and the solvent (12). CAN brought about the conversion of epoxides into β-nitrato alcohols in the presence of an excess of nitrate ion (12*a*–12*b*). Recently, it was reported that CAN mediated ring opening of cyclopropyl alcohols and specifically gave β-functionalized ketones in the presence of selected anions (13). The substitutent-dependent fashion in the NO-mediated ring-opening reaction of epoxides (4) stimulated us to explore whether a similar effect also exists in the ring-opening reaction of epoxides with CAN. In addition, the resulting vicinal alcohols from the ring-opening reaction of epoxides will be important intermediates in organic synthesis (14).

Received 24 September 2007. Accepted 4 December 2007. Published on the NRC Research Press Web site at canjchem.nrc.ca on 17 January 2008.

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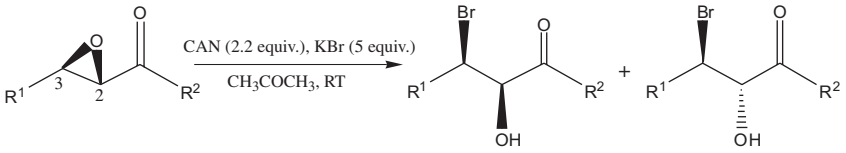
Result and discussion

In the present work, *trans* chalcone epoxides were employed as substrates. We started with α,β-epoxy phenyl ketones **1**, which were easily prepared by the reaction of chalcone with H_2O_2. Upon treatment of 1 equiv. of **1** with 2.2 equiv. of CAN and 5 equiv. of KBr in acetone at room temperature (RT), ring-opening reactions occurred regioselectively at the β-C and brominations specifically at the β-C, giving β-bromo-α-hydroxyl ketones **2** in moderate yields (Scheme 1 and Table 1). All products were characterized by IR, MS, HRMS, ^1H, and ^{13}C NMR. Weber first synthesized chalcone bromohydrins using $SnBr_4$ in 1992. He determined his products to be syn configurations mainly by NMR parameters (15). As such, the configuration of products **2** was confirmed to be dominantly syn (4*a*, 15, 16).

It was also found that CAN and KBr acted cooperatively to cause the ring-opening reactions. No ring-opening reaction occurred in the absence of either CAN or KBr. Furthermore, the reaction proceeded very slowly when a catalytic amount of CAN was applied. One reason for this may be partially attributed to polar substituted epoxides having less activity toward the ring-opening reaction (12*d*). Although the reaction mechanism is far from clear, a possible pathway for the present ring-opening reaction and bromination may be rationalized in terms of bromine radical, which is formed by the oxidation of bromide ion with an excess amount of CAN (13, 17) and the subsequent addition of bromine radical to three-membered epoxide ring (10a, 18), leading to the ring opening. On reviewing previous works on similar topics (4, 19), it is found that the carbonyl group plays a key role in ring-opening regioselectivity. The carbonyl group causes

 doi:10.1139/V07-148

Scheme 1.



1 ***syn*-2** ***anti*-2**

dr of *syn* to *anti* up to 99:1

Table 1. Ring opening of 2,3-epoxy phenyl ketones with CAN and KBr in acetone.

Substrate	R^1	R^2	Time (h)	Yield (%)[a]	dr syn:anti (%)[b]
1a	Ph	Ph	10	77	> 99:1
1b	Ph	(p)-Br-Ph	18	73	88:12
1c	Ph	(p)-F-Ph	18	70	87:13
1d	(p)-MeO-Ph	Ph	0.1	0[c]	—
1e	(p)-Me-Ph	Ph	3	76[d]	90:10
1f	(p)-Cl-Ph	Ph	16	80	> 99:1
1g	(p)-Cl-Ph	(p)-Br-Ph	16	76	87:13
1h	(p)-Cl-Ph	(p)-MeO-Ph	14	85	96:4
1i	(p)-O_2N-Ph	Ph	24	51	70:30
1j	(p)-O_2N-Ph	(p)-MeO-Ph	20	71	77:23
1k	(m)-O_2N-Ph	Ph	24	58	73:27

[a]Yields refer to isolated products.
[b]The ratio of *syn*-**2** to *anti*-**2** was evaluated using the characteristic ^{1}H NMR peaks both of α- and β-H, such as in **2j**, 5.56 (*syn*-α-H) to 5.41 ppm (*anti*-α-H) as well as 5.33 (*syn*-β-H) to 5.10 (*anti*-β-H).
[c]Material decomposed in 5 min, giving 91% of 4-methoxybenzaldehyde.
[d]Along with 55% of 4-methylbenzaldehyde.

the ring opening uniquely at β-C, yet the stereochemistry strongly depends on reaction conditions. The assumption of a one-electron transfer reaction between epoxide and Ce(IV), with a catalytic amount leading to the formation of an expoxonium radical cation (12*b*–12*e*), will be ruled out in the present case.

The effect of solvents on this reaction was examined using **1a** as a substrate (Table 2). From Table 2 we can find that some aprotic solvents such as acetone and THF were the most favorable solvents, whereas CH_2Cl_2 disfavored the ring-opening reaction. In general, CAN is insoluble in organic solvents. If a small amount of water is contained in solvents, then the solvent polarity somewhat affects the solubility of CAN in reaction media. Otherwise, protic solvents would join the reaction (12*c*, 19*a*), as in the case of methanol (Table 2).

In summary, we have developed an efficient method for the regioselective and syn-selective conversion of *trans* chalcone epoxides to *syn* chalcone bromohydrins by CAN and potassium bromide.

Table 2. Effect of solvents on the yield of **2a**.

Solvent	Yield of **2a** (%)
CH_3COCH_3	77
CH_3CN	60
THF	66
Et_2O	64
CH_3COOEt	33
CH_2Cl_2	0
CH_3OH	19[a]

Note: The ratio of syn to anti in all solvents was ca. 99:1.
[a]Along with 75% of 2-hydroxy-3-methoxy-1,3-diphenylpropan-1-one (19*a*).

Experimental

General

Flash chromatography was carried out using silica gel 60 (200–300 mesh, particle size 0.040–0.062 mm) supplied by Qingdao Ocean Chemical Plant. Melting points were measured with a digital Koffer apparatus and were uncorrected. IR (KBr) analysis of solid compounds was performed on a Nicolet NEXUS 670 FT-IR spectrophotometer and reported in cm^{-1}. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury Plus 300 MHz NMR spectrometer. Chemical shifts (δ) for ^{1}H and ^{13}C NMR spectra are reported in parts per million (ppm) from solvent $CDCl_3$ (7.26 ppm) and (77.0 ppm), respectively, as internal standards relative to tetramethylsilane. MS data were obtained with EI (70 eV) on an HP-5988 spectrometer by direct inlet at 70 eV. HRMS data was obtained on a Bruker Daltonics APEX FT-ICR spectrometer. Chemicals were of highest grade commercially available and used as received, unless otherwise stated. All reagents were weighed and handled in air at RT.

Typical procedure for the preparation of 1a

To a solution of 1.040 g of chalcone (5 mmol) in 25 mL of methanol were added 1.035 g of K_2CO_3 (7 mmol) and

2 mL of H_2O_2 (30%). The mixture was stirred at ambient temperature until a white precipitate appeared, then isolated by filtration with the aid of Celite, and washed with water, affording **1a**. Other substrates were prepared by similar procedures.

Typical procedure for the ring-opening reaction of 1a with CAN and KBr

To a solution of 0.112 g (0.5 mmol) of **1a** in 15 mL of acetone were added 0.300 g of KBr (2.5 mmol) and 0.600 g of CAN (1.1 mmol). The mixture was stirred at ambient temperature until the reaction completed, water then added to dissolve the salts, and extracted with 3 × 10 mL Et_2O. The organic layer was dried over anhyd. Na_2SO_4, filtered, concentrated under vacuum, and purified by flash column chromatography on silica gel (petroleum ether/acetic ether 10:1), giving pure **2a**. All compounds were recrystalized from petroleum ether (60–80 °C)-acetic ether. Other ring-opening reactions were performed accordingly.

Characterization data for products

Syn-2a (15)

Yellow solid, yield 77%, mp 90–92. IR (KBr, cm^{-1}) ν: 3472, 1673, 1271, 977. ^1H NMR (300 MHz, $CDCl_3$, ppm) δ: 7.85 (d, *J* = 7.2 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, *J* = 7.8 Hz, 1H), 7.50 (m, *J* = 7.5 Hz, *J* = 7.8 Hz, 2H), 7.18–7.23 (m, 5H), 5.59 (dd, *J* = 3.9 Hz, *J* = 7.2 Hz, 1H), 5.34 (d, *J* = 3.9 Hz, 1H), 3.73 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ: 197.2, 135.8, 134.4, 134.2, 129.0, 128.9, 128.7, 128.6, 128.2, 76.9, 53.4. EI-MS *m/z*: 306 [M + 2], 304 [M^+], 224, 135. HRMS *m/z* calcd. for $C_{15}H_{13}O_2Br$ [M + Na]$^+$: 326.9991; found: 326.9995.

2b (15) (Obtained as a mixture 7:1 syn/anti isomers)

Yellow solid, yield 73%, mp 128–130. IR (KBr, cm^{-1}) ν: 3489, 1677, 1300, 860. ^1H NMR (300 MHz, $CDCl_3$, ppm) δ: 7.87 (d, *J* = 9.0 Hz, 0.4H), 7.72 (d, *J* = 9.0 Hz, 2H), 7.63 (d, *J* = 9.0 Hz, 2H), 7.46 (d, *J* = 9.0 Hz, 0.4H), 7.38 (d, *J* = 9.0 Hz, 0.4H), 7.33 (m, 2H), 7.23 (m, 3H), 5.72 (d, *J* = 8.1 Hz, 0.16H), 5.53 (d, *J* = 3.6 Hz, 1.1H), 5.31 (d, *J* = 3.6 Hz, 0.98H), 5.15 (d, *J* = 8.1 Hz, 0.14H), 3.73 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ: 196.5, 135.8, 133.0, 132.2, 131.3, 130.1, 129.3, 128.4, 127.2, 77.6, 53.2. MS-EI *m/z*: 304 [M – HBr], 303 [M – Br], 305, 302, 215, 213.

2c (15) (Obtained as a mixture 6.7:1 syn/anti isomers)

Yellow solid, yield 70%, mp 98–101. IR (KBr, cm^{-1}) ν: 3510, 1680, 1270, 863. ^1H NMR (300 MHz, $CDCl_3$, ppm) δ: 8.05 (t, *J* = 8.1 Hz, 0.17H), 7.89 (t, *J* = 8.1 Hz, 1.4H), 7.48 (t, *J* = 8.1 Hz, 0.6H), 7.46–7.15 (m, 7.7H), 6.87 (t, *J* = 8.1 Hz, 0.35H), 5.75 (d, *J* = 8.1 Hz, 0.15H), 5.53 (d, *J* = 4.2 Hz, 1H), 5.29 (d, *J* = 4.2 Hz, 1H), 5.20 (d, *J* = 8.1 Hz, 0.16H), 3.91 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ: 195.8, 167.9, 135.9, 131.4, 130.5, 128.7, 128.4, 127.2, 116.3, 76.3, 53.3. MS-EI *m/z*: 322 [M^+], 324 [M + 2], 306, 304, 169, 171, 153.

2e (15) (Obtained as a mixture 9.5:1 of syn/anti isomers)

Yellow solid, yield 76%, mp 88–91. IR (KBr, cm^{-1}) ν: 3480, 1658, 1266, 810. ^1H NMR (300 MHz, $CDCl_3$, ppm) δ: 7.92 (d, *J* = 8.1 Hz, 0.2H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.70 (d, *J* = 8.1 Hz, 0.12H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.53 (d, *J* = 8.1 Hz, 0.2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 0.2), 7.13 (d, *J* = 8.1 Hz, 2H), 7.07 (d, *J* = 8.1 Hz, 0.2H), 6.08 (d, *J* = 4.2 Hz, 1H), 5.81 (d, *J* = 8.1 Hz, 0.11H), 5.54 (d, *J* = 8.1 Hz, 0.11H), 5.37 (d, *J* = 4.2 Hz, 1H), 4.11 (s, 1H), 2.35 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ: 197.5, 139.3, 133.7, 130.8, 129.2, 128.6, 128.3, 127.8, 127.0, 84.3, 74.2, 21.1. MS-EI *m/z*: 318 [M^+], 320 [M + 2], 239 [M – Br], 238 [M – HBr].

Syn-2f (15)

Yellow solid, yield 80%, mp 93–95. IR (KBr, cm^{-1}) ν: 3512, 1692, 1280, 836. ^1H NMR (300 MHz, $CDCl_3$, ppm) δ: 7.84 (d, *J* = 7.5 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.45 (d, *J* = 7.5 Hz, 2H), 7.17 (m, 4H), 5.57 (d, *J* = 3.0 Hz, 1H), 5.30 (d, *J* = 3.0 Hz, 1H), 3.84 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ: 196.9, 134.7, 134.5, 134.4, 133.8, 129.9, 129.2, 128. 6, 128.4, 76.8, 52.1. MS-EI *m/z*: 338 [M^+], 340 [M + 2], 259 [M – Br], 258 [M – HBr], 261, 260.

2g (New compound obtained as a mixture 6.7:1 of syn/anti isomers)

Yellow solid, yield 76%, mp 140–142. IR (KBr, cm^{-1}) ν: 3510, 1688, 1276, 830. ^1H NMR (300 MHz, $CDCl_3$, ppm) δ: 7.86 (d, *J* = 8.4 Hz, 0.6 H), 7.70 (dd, *J* = 8.4 Hz, *J* = 8.4 Hz, 4H), 7.37 (d, *J* = 8.4 Hz, 0.6H), 7.21 (dd, *J* = 8.4 Hz, *J* = 8.4 Hz, 4H), 5.49 (d, *J* = 3.9 Hz, 1H), 5.30 (d, *J* = 9.0 Hz, 0.16H), 5.22 (d, *J* = 3.9 Hz, 1H), 5.06 (d, *J* = 8.7 Hz, 0.15H), 3.70 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ: 196.3, 134.9, 134.4, 132.7, 132.5, 132.2, 130.4, 130.1, 128.5, 76.7, 51.9. MS-EI *m/z*: 337 [M – Br], 336 [M – HBr], 338, 339. HRMS *m/z* calcd. for $C_{15}H_{11}O_2ClBr_2$ [M + Na]$^+$: 440.8398; found: 440.8392.

2h (New compound obtained as a mixture 25:1 of syn/anti isomers)

Yellow solid, yield 85%, mp 88–90. IR (KBr, cm^{-1}) ν: 3515, 1684, 1286, 836. ^1H NMR (300 MHz, $CDCl_3$, ppm) δ: 7.83 (d, *J* = 8.7 Hz, 2H), 7.17 (m, 3H), 6.98 (t, *J* = 8.7 Hz, 3H), 5.73 (d, *J* = 8.1 Hz, 0.06H), 5.50 (d, *J* = 3.6 Hz, 1H), 5.27 (d, *J* = 3.6 Hz, 1H), 5.11 (d, *J* = 8.1 Hz, 0.04H), 3.91 (s, 3H), 3.82 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ: 194.9, 164.6, 134.5, 131.0, 129.9, 128.8, 128.2, 126.5, 114.3, 76.2, 55.5, 52.5. MS-EI *m/z*: 289 [M – Br], 288 [M – HBr], 291, 290, 135. HRMS *m/z* calcd. for $C_{16}H_{15}O_3ClBr$ [M + Na]$^+$: 392.9868; found: 392.9862

2i (New compound obtained as a mixture 2.3:1 of syn/anti isomers)

Yellow solid, yield 51%, mp 112–115. IR (KBr, cm^{-1}) ν: 3530, 1705, 1355, 844. ^1H NMR (300 MHz, $CDCl_3$, ppm) δ: 8.22 (d, *J* = 8.1 Hz, 1H), 8.04 (m, 2H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.49 (m, 3H), 7.36 (d, *J* = 8.1 Hz, 1H), 5.61 (d, *J* = 4.2 Hz, 0.7H), 5.41 (d, *J* = 8.4 Hz, 0.3H), 5.26 (d, *J* = 4.2 Hz, 0.7H), 5.14 (d, *J* = 8.4 Hz, 0.3H), 3.89 (s, 1.38H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ: 197.2, 193.5, 148.2, 146.3, 144.7, 142.3, 134.5, 133.3, 133.1, 132.7, 128.4, 128.1, 127.5, 127.1, 119.4, 119.1, 76.3, 74.5, 55.2, 52.8. MS-EI *m/z*: 270 [M – Br], 269 [M – HBr], 165, 105. HRMS *m/z* calcd. for $C_{15}H_{12}O_4NBr$ [M + H]$^+$: 351.0111; found: 351.0115.

2j (New compound obtained as a mixture 3.3:1 of syn/anti isomers)

Yellow solid, yield 71%, mp 103–105. IR (KBr, cm^{-1}) ν: 3518, 1695, 1338, 835. ^1H NMR (300 MHz, $CDCl_3$, ppm) δ: 8.22 (d, *J* = 8.7 Hz, 0.6H), 8.06 (d, *J* = 8.7 Hz, 2H), 7.97 (d, *J* = 8.7 Hz, 0.7H), 7.86 (d, *J* = 8.7 Hz, 2H), 7.66 (d, *J* = 8.7 Hz, 0.6H), 7.37 (d, *J* = 8.7 Hz, 2H), 7.00 (d, *J* = 8.7 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 0.6H), 5.56 (d, *J* = 3.6 Hz, 1H), 5.41 (d, *J* = 8.1 Hz, 0.3H), 5.33 (d, *J* = 3.3 Hz, 1H), 5.10 (d, *J* = 8.1 Hz, 0.3H), 3.91 (s, 4H), 3.87 (s, 1.2H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ: 194.7, 191.1, 164.9, 147.8, 142.9, 131.5, 131.2, 129.7, 128.4, 126.2, 123.5, 123.2, 114.6, 114.2, 109.7, 76.1, 55.7, 51.4. MS-EI *m/z*: 301 [M – Br], 299 [M – HBr], 165, 135. HRMS *m/z* calcd. for $C_{16}H_{14}O_5NBr$ $[M + H]^+$: 381.0214; found: 381.0219.

2k (New compound obtained as a mixture 2.8:1 of syn/anti isomers)

Yellow solid, yield 58%, mp 86–88. IR (KBr, cm^{-1}) ν: 3528, 1712, 1357, 720. ^1H NMR (300 MHz, $CDCl_3$, ppm) δ: 8.12 (m, 4H), 7.88 (m, 2H), 7.68 (m, 1H), 7.53 (m, 6H), 5.61 (d, *J* = 4.2 Hz, 1H), 5.42 (d, *J* = 8.4 Hz, 0.38H), 5.38 (d, *J* = 4.2 Hz, 1H), 5.19 (d, *J* = 8.4 Hz, 0.36H), 3.97 (s, 1.4H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ: 197.0, 193.8, 148.0, 147.8, 138.0, 134.5, 134.3, 134.0, 129.8, 129.6, 128.4, 128.1, 127.8, 123.7, 123.4, 122.0, 76.4, 73.8, 51.0, 47.5. MS-EI *m/z*: 270 [M – Br], 269 [M – HBr], 165, 105. HRMS *m/z* calcd. for $C_{15}H_{12}O_4NBr$ $[M + H]^+$: 351.0111; found: 351.0108.

Acknowledgement

Project 20572040 was supported by National Natural Science Foundation of China.

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