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Co(III) catalysed asymmetric ring-opening of epichlorohydrin by salicylaldehyde derivatives: reversal of enantioselectivity and rate acceleration on addition of $AlCl_3$

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Using asymmetric Cobalt(III) salen catalysts, the ring-opening of epichlorohydrin by 2,3-dihydroxybenzaldehyde and 2,4- dihydroxybenzaldehyde was found to occur at the phenolic groups most distant from the aldehydic group. Switching catalysts afforded a reversal in enantioselectivity. For 2,3-dihydroxybenzaldehyde and salicylaldehyde, addition of $AlCl_3$ to the reaction mixture led to an increase in reaction rate without any decrease in product enantiopurity.

Key Words: Asymmetric catalysis; salicylaldehyde; Co(III) salen; aryloxy alcohols; epoxide ring-opening

Introduction

The reaction between phenols and epoxides is an attractive route to synthetically useful α-aryloxy alcohols.[1,2] However, by comparison with other substrates such as alcohols,[3] amines,[4] thiols,[5] or carboxylic acids[6] this ring-opening reaction does not proceed readily and traditionally harsher reaction conditions have been used which involve formation of phenoxide anions.[7−10] Nonetheless, asymmetric ring-opening of epoxides by phenols was first reported in the late 1990s. These initial reports involved ring-opening of meso epoxides by p-methoxyphenol catalysed by heterobimetallic gallium bis(napthoxide) complexes[11] and kinetic resolution of racemic epoxides using Jacobsen's asymmetric cobalt(III) catalyst (**1a**),[12] which is depicted in Figure. The latter reaction could readily be applied to unsubstituted or para substituted phenols.[13] However, the reaction with less active ortho-substituted phenols required more active oligomeric catalysts[14,15] which required multi-step synthesis.

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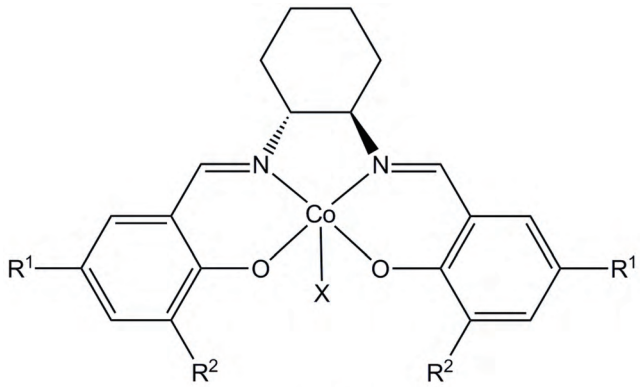
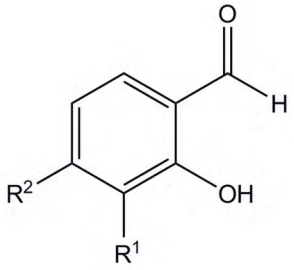


(R,R)-**1a** ($R^1 = R^2 =$ t-Bu, X = OAc)
(R,R)-**1b** (R^1 = t-Bu, R^2 = H, X = OAc)



2a (R^1 = H, R^2 = OH)
2b (R^1 = OH, R^2 = H)
2c (R^1 = H, R^2 = H)

Figure. The catalysts and substrates used in this study.

More recently Kim and coworkers reported that a heterobimetallic catalyst prepared from 5-t-bu substituted catalyst (**1b**, X = 4-nitrobenzenesulfonate) and $AlCl_3$ could afford high enantiomeric excesses of meta substituted phenols and that this type of catalyst was more active than a similar catalyst prepared from **1a**.[16] Although the exact structure of these catalysts may not be completely clear, it appears reasonable that catalyst **1b** would on steric grounds allow more rapid reactivity than the 3,5-di-t-butyl catalyst (**1a**) and therefore catalyst **1b** seems as though it may be a good candidate for reactions with less active ortho-substituted phenols. In addition, it also seems reasonable that addition of Lewis acids such as $AlCl_3$ may also be useful for increasing the reactivity of less active substrates. As salicylaldehyde based compounds are ubiquitous in metal-ligand chemistry and have many applications, we thought that it would be interesting to attempt the ring-opening reaction of epoxides by salicylaldehyde derivatives using catalysts **1a** and **1b** and to observe the effect of added $AlCl_3$ in these reactions. We report here our findings that catalyst **1b** can indeed impart considerably greater reactivity than the 3,5-di-t-butyl catalyst for sterically hindered OH groups. However, an unexpected reversal of enantioselectivity was observed. Furthermore, addition of $AlCl_3$ to the reaction mixture showed no adverse effect on enantioselectivity but in some cases showed significant rate acceleration.

Experimental

All ^{1}H-NMR and ^{13}C-NMR spectra were recorded using a Varian AS 400+ Mercury FT NMR spectrometer at ambient temperature. IR spectra were recorded as either KBr discs or thin films between NaCl plates on a Perkin Elmer 1600 FTIR spectrometer. Molecular sieves were powdered and dried in a vacuum oven at 130 ^{o}C. HPLC analyses were performed using a chiralcel OD-H column. Solvents were used as received from commercial suppliers. Catalysts **1a** and **1b** were prepared according to the literature method.[17]

Reactions of aldehydes with epichlorohydrin

The aldehyde (1.0 equiv.) and epichlorohydrin (2.1 equiv.) were added to **1a** or **1b** (0.05 equiv for **2a** and **2b**; 0.1 equiv for **2c**) and molecular sieves (3A, 100 mg). In some instances, an amount of $AlCl_3$ (equimolar

to the amount of catalyst) was also added. Tert-butylmethyl ether (TBME) (0.15 mL) was added to the stirred mixture and stirring was continued at the specified temperature until TLC monitoring showed complete disappearance of the aldehyde. The solvent was then removed and the pure products were obtained by subjecting the obtained residues to Si gel column chromatography eluting with a n-hexane/ethyl acetate (2:1) solvent system. Absolute configurations of the products were determined by repeating the experiments using epichlorohydrin that had been resolved by hydrolytic kinetic resolution.[18] The products were characterised by standard techniques and their structures were further confirmed by derivatization as oximes. For products **3a** and **3b**, cyclisation of the resultant oximes to afford benzisoxazoles was also carried out. 4-(3-chloro-2-hydroxypropoxy)-2-hydroxybenzaldehyde (**3a**); mp 93.1-94.8 ^{o}C; ^{1}H-NMR ($CDCl_3$)δ(ppm): 11.36 (s, 1H), 9.66 (s, 1H), 7.38 (d, J= 8.8 Hz, 1H), 6.49 (dd, J= 8.4, 2.4 Hz, 1H), 6.38 (d, J= 2.4 Hz, 1H), 4.18 (m, 1H), 4.07 (d, J= 5.6 Hz, 2H), 3.68 (m, 2H), 2.52 (br, 1H); ^{13}C-NMR ($CDCl_3$)δ: 194.74, 165.50, 164.58, 135.67, 115.87, 108.58, 101.80, 69.75, 69.14, 46.01 ppm. IR (KBr): 3381, 1672, 1601 cm^{-1}. Anal. Calcd. for $C_{10}H_{10}ClO_4$: C, 52.05; H, 4.81. Found: C, 51.75; H, 4.00%. 3-(3-chloro-2-hydroxypropoxy)-2-hydroxybenzaldehyde (**3b**); ^{1}H-NMR ($CDCl_3$)δ(ppm): 11.12 (s, 1H), 9.92 (s, 1H), 7.24 (dd, J= 7.6, 1.6 Hz, 1H), 7.18 (dd, J= 8, 1.6 Hz, 1H), 6.96 (t, J= 7.6 Hz, 1H), 4.24 (m, 1H), 4.17 (d, J= 4.8 Hz, 2H), 3. 77 (m, 2H); ^{13}C-NMR ($CDCl_3$)δ: 196.68, 152.13, 147.27, 126.14, 120.03, 121.56, 121.51, 71.22, 70.11, 45.52 ppm. IR (NaCl): 3424, 2961, 2932, 1726 cm^{-1}. Anal. Calcd. for $C_{10}H_{10}ClO_4$: C, 52.05; H, 4.81. Found: C, 51.75; H, 5.05%. 2-(3-chloro-2-hydroxypropoxy)benzaldehyde (**3c**). ^{1}H-NMR ($CDCl_3$)δ(ppm): 10.38 (s, 1H), 7.80 (dd, J= 7.6, 2.8 Hz, 1H), 7.54 (m, 1H), 7.06 (dd, J= 7.6, 1.5 Hz, 1H), 7.02 (d, J= 8.0 Hz, 1H), 3.77 (t, J= 4.8 Hz, 1H), 3.71 (d, J= 5.2 Hz, 2H), 3. 21 (s, 1H), 1.28 (m, 1H); ^{13}C-NMR ($CDCl_3$)δ: 190.09, 160.50, 136.30, 130.35, 125.35, 121.77, 113.32, 69.89, 69.69, 45.85 ppm. IR (NaCl): 3416, 2879, 1688, 1030 cm^{-1}. MS (ESI) calcd. for $C_{10}H_{10}ClO_3Na$ (M+Na^{+}): 237. Found: 237.

Preparation of oximes

The oximes were prepared using a procedure similar to reported methods.[19] A 5 mL solution of $NH_2OH.HCl$ (0.34 mmol) and CH_3COONa (0.34 mmol) in water was added dropwise to a solution of the appropriate aldehyde (0.33 mmol) in 2 mL of ethanol. The resulting solution was stirred at room temperature for 3 h. Ethanol was evaporated and the product was extracted with TBME (3 $\times$ 5 mL). The combined organic phases were dried (Na_2SO_4) and concentrated to afford the crude product. The pure products were crystallized from dichloromethane/hexane to afford white solids. 4-(3-chloro-2-hydroxypropoxy)-2-hydroxybenzaldoxime (**4a**) (79% yield); mp 102-105.2 ^{o}C; ^{1}H-NMR (DMSO) δ(ppm): 8.23 (s, 1H), 7.35 (d, J= 8.8 Hz, 1H), 6.47 (dd, J= 8.8, 2.8 Hz, 1H), 6.43 (d, J= 2.4 Hz, 1H), 4.00 (m, 1H), 3.95 (m, 2H), 3.67 (m, 2H); ^{13}C-NMR (DMSO) δ: 161.03, 158.26, 148.61, 130.06, 112.20, 107.20, 69.75, 69.23, 47.31 ppm. IR (KBr): 3379, 1621 cm^{-1}. Anal. Calcd. for $C_{10}H_{12}ClNO_4$: C, 48.89; H, 4.92; N, 5.70. Found: C, 48.46; H, 4.82; N, 5.76%. 3-(3-chloro-2-hydroxypropoxy)-2-hydroxybenzaldoxime (**4b**) (91% yield); mp 100-103 ^{o}C; ^{1}H-NMR ($CDCl_3$)δ(ppm): 10.3 (bs, 1H), 8.22 (s, 1H), 7.01 (dd, J= 7.2, 2.4 Hz, 1H), 6.88 (m, 2H), 4.23 (m, 1H), 4.18 (d, J= 4.8 Hz, 2H), 3.75 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ: 152.45, 147.66, 147.05, 124.14, 120.17, 117.68, 117.50, 71.89, 70.35, 45.20 ppm. IR (KBr): 3395, 3256, 1579, 1479 cm^{-1}. Anal. Calcd. for $C_{10}H_{12}ClNO_4$: C, 48.89; H, 4.92; N, 5.70. Found: C, 48.87; H, 4.83; N, 5.85%. (**4c**) (88% yield); mp 100-103 ^{o}C; ^{1}H-NMR ($CDCl_3$)δ(ppm): 8.36 (s, 1H), 7.65

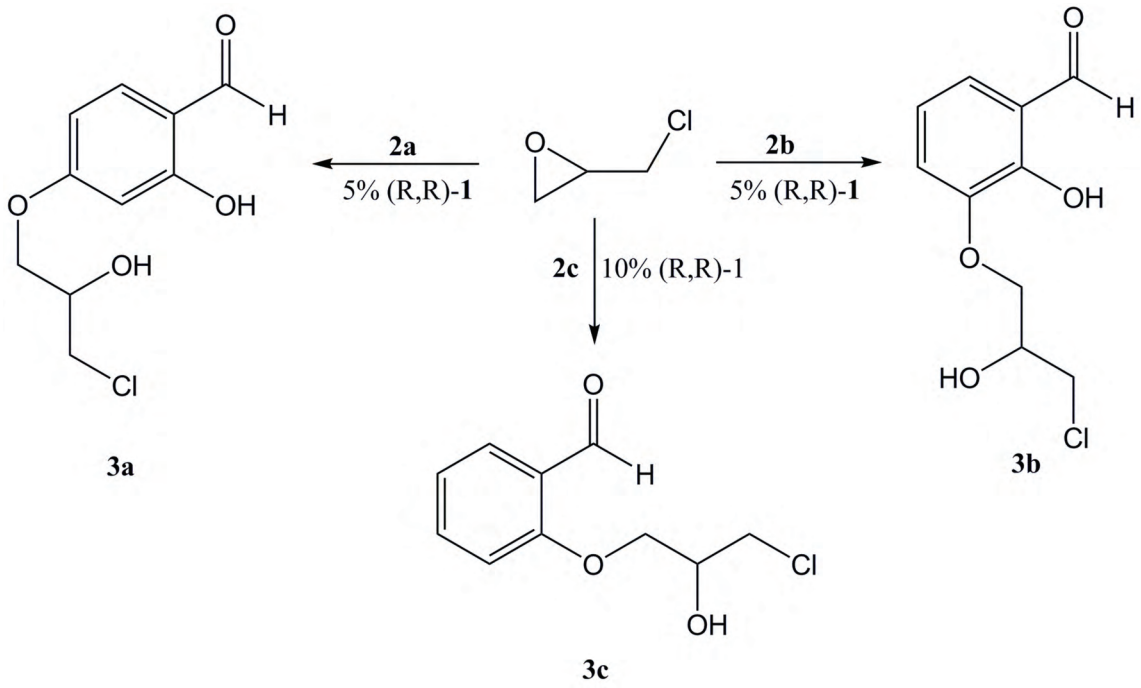
(dd, J= 7.6, 1.6 Hz, 1H), 7.33 (m, 1H), 7.05 (d, J= 8.0 Hz, 1H), 6.95 (d, J= 7.2 Hz, 1H), 4.03 (m, 4H), 3.70 (m, 2H); ^{13}C-NMR ($CDCl_3$)δ: 165.68, 144.29, 131.41, 126.10, 122.07, 121.63, 113.52, 70.34, 69.34, 47.27 ppm. IR (KBr): 3390, 3251, 1570 cm^{-1}. Anal. Calcd. for $C_{10}H_{12}ClNO_3$: C, 52.30; H, 5.27; N, 6.10. Found: C, 51.96; H, 5.18; N, 5.69%.

Preparation of benzisoxazoles

Cyclisation of the oximes was carried out using the literature procedure.[20] A mixture of triphenylphosphine (0.49 mmol) and 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) (0.49 mmol) in dry dichloromethane (5 mL) was stirred at room temperature for 1 min. Salicylaldoxime (0.33 mmol) was then added. TLC monitoring showed completion of the reaction. The solvent was evaporated. Column chromatography of the crude mixture on silica gel using n-hexane and ethyl acetate (3:1) as eluent gave the desired products as white solids. 6-(3-chloro-2-hydroxypropoxy)-1,2-benzisoxazole (**5a**) (86% yield); mp 79.4-82 ^{o}C; ^{1}H-NMR ($CDCl_3$)δ(ppm): 8.59 (s, 1H), 7.59 (d, J= 8 Hz, 1H), 7.08 (s, 1H), 6.97 (dd, J= 8.8, 2.4 Hz, 1H), 4.28 (m, 1H), 4.18 (m, 2H), 3.79 (m, 2H); ^{13}C-NMR ($CDCl_3$)δ: 164.12, 161.04, 146.03, 122.58, 115.51, 114.88, 93.76, 69.89, 69.36, 46.10 ppm. Anal. Calcd. for $C_{10}H_{10}ClNO_3$: C, 52.76; H, 4.43; N, 6.15. Found: C, 52.39; H, 4.41; N, 6.22%. IR (KBr): 3371, 1618 cm^{-1}. 7-(3-chloro-2-hydroxypropoxy)-1,2-benzisoxazole (**5b**) (39% yield); mp 63-65 ^{o}C; ^{1}H-NMR ($CDCl_3$)δ(ppm): 8.70 (s, 1H), 7.34 (d, J= 8 Hz, 1H), 7.24 (t, J= 7.6 Hz, 1H), 7.05 (d, J= 7.6 Hz, 1H), 4.39 (s, 1H), 4.37 (d, J= 4 Hz, 2H), 4.34 (m, 1H), 3.84 (m, 2H); ^{13}C-NMR ($CDCl_3$)δ: 153.06, 146.62, 143.31, 125.17, 123.73, 114.68, 113.29, 70.31, 70.02, 45.98 ppm. Anal. Calcd. for $C_{10}H_{10}ClNO_3$: C, 52.76; H, 4.43; N, 6.15. Found: C, 52.32; H, 4.55; N, 6.03%. IR (KBr): 3399, 2927, 1607, 1532, 1467 cm^{-1}.

Results and discussion

The ring-opening reactions of epichlorohydrin that were carried out can be seen in Scheme 1. Initial reactions were carried out using aldehyde (**2a**) and these results are given in Table 1. In these experiments, the rates of the reaction for both catalysts (**1a**) and (**1b**) were very similar. Thus, the reactions were completed within approximately 24 h at room temperature to give a single product arising from selective reaction at the 4-OH group. This was determined from ^{1}H-NMR spectra of the product where the characteristic low field signal of the 2-OH group could be observed at δ 9.0 ppm. It was further confirmed by conversion of the product to the corresponding 1,2-benzisoxazole (**5a**) (Scheme 2). Surprisingly, very poor enantioselectivity was observed for catalyst **1a**. When using catalyst **1b**, enantioselectivity was increased, but, in a further surprise, the major enantiomer in this case was the S enantiomer, not the expected R enantiomer. This surprising enantioselectivity clearly suggests that substrate **2a** is not activated by catalysts **1** in the same way that simple phenols are.[21] Decreasing the reaction temperature rapidly decreased rates of reaction but afforded only a small increase in enantiomeric excess. Addition of $AlCl_3$ to the reaction mixture caused no difference in reaction rates. This observation is consistent with the results of Song et al., who have suggested that Lewis acids such as $AlCl_3$ do not form bimetallic catalysts with Co(III)salen complexes under these conditions and have no effect on the hydrolytic kinetic resolution of epoxides.[22]



Scheme 1. Ring-opening of epichlorohydrin by salicylaldehyde derivatives using catalysts **1a** and **1b**.

Table 1. Yields and optical activities obtained in the catalytic asymmetric ring-opening of epichlorohydrin by **2a**[a].

Substrate	Catalyst (5 mol%)	$AlCl_3$ (mol%)	Temp.	Time	Yield[b]	ee[c] (%)
2a	**1a**	-	RT	22h	87	5(R)
2a	**1a**	-	0 ^oC	11d	33	3(R)
2a	**1a**	5	0 ^oC	11d	41	4(R)
2a	**1a**	5	RT	43h	69	4(R)
2a	**1b**	-	RT	24h	80	30(S)
2a	**1b**	-	0 ^oC	11d	52	38(S)
2a	**1b**	5	0 ^oC	11d	50	40(S)
2a	**1b**	5	RT	43h	66	15(S)

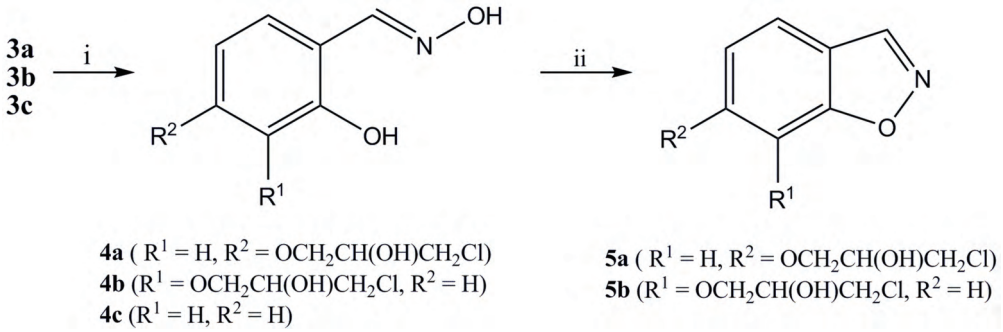
[a]reactions run in TBME.

[b]isolated yields after column chromatography based on **2a**.

[c]determined by chiral HPLC analysis. Major enantiomer in parentheses.

Using 2,3-dihydroxybenzaldehyde, a different set of results was obtained (Table 2). For these reactions no significant amount of product was obtained after 30 days using only catalyst **1a** or **1b**. This suggests that both phenolic groups may be too sterically encumbered to be sufficiently activated by either Co(III) salen catalyst. However, if a catalytic amount of $AlCl_3$ was added, good conversion to product was obtained within 1 to 4 days. This represents a dramatic rate acceleration. Confirmation that reaction occurred cleanly at the 3-OH position was again obtained from ^{1}H-NMR and conversion of the product to the corresponding benzisoxazole.

Enantioselectivities were greater than in the case of 2,4-dihydroxybenzaldehyde. Again, catalyst **1b** afforded the S enantiomer as the major steroisomer whereas catalyst **1a** afforded the R enantiomer as the major isomer. Upon cooling the temperature, reaction rates decreased significantly but the optical purities of the product increased. Thus, in this case it appears as though the phenolic groups may be activated by the Lewis acidic $AlCl_3$ but not by the Co(III) salen catalyst. Indeed, considering the well-known ability of $AlCl_3$ to coordinate to aromatic diol groups such as catechol[23] or binol,[24] it seems likely that $AlCl_3$ may coordinate to the diol part of the substrate aldehyde. Although the related catechol borates are capable of ring-opening epoxides in the absence of transition-metal catalysts,[25] in this case it is clear that the chiral Co(III) salen catalyst also must have a role to play; otherwise the product would be obtained in racemic form. Therefore, it seems likely that when 2,3-dihydroxybenzaldehyde is the substrate, the epoxide group is activated by coordination to the Co(III) salen catalyst whereas the phenol group is activated by coordination to $AlCl_3$. This proposal is consistent with the generally accepted mechanism for Co(III) salen catalysed reactions in which the attacking nucleophile and the epoxide are thought to be activated by separate metal centres.[26]



Scheme 2. Synthesis of oximes and benzisoxazoles. Reagents and conditions: (i)$NH_2OH.HCl$, CH_3COONa, EtOH, RT; (ii) PPh_3, DDQ, CH_2Cl_2, RT.

Table 2. Yields and optical activities obtained in the catalytic asymmetric ring-opening of epichlorohydrin by **2b**[a].

Substrate	Catalyst (5 mol%)	$AlCl_3$ (mol%)	Temp.	Time	Yield[b]	ee[c] (%)
2b	**1a**	5	RT	4d	39	35(R)
2b	**1a**	5	0 ^oC	11d	29	50(R)
2b	**1b**	5	RT	2d	58	47(S)
2b	**1b**	5	0 ^oC	9d	31	70(S)

[a] reactions run in TBME.

[b]isolated yields after column chromatography based on **2b**.

[c]determined by chiral HPLC analysis. Major enantiomer in parentheses.

Using salicylaldehyde, in the absence of $AlCl_3$, the reaction using catalyst **1a** was so slow that no isolable amount of product could be obtained after 1 month at RT (Table 3). In contrast, using catalyst **1b**, a moderate yield of product could be obtained after 3 days. When $AlCl_3$ was added, a significant rate acceleration was observed for catalyst **1a**. Thus, within 6 days a moderate yield of product was obtained. However, no increase in reaction rate was observed when catalyst **1b** was used. As with aldehydes **2b** and **2c**, when catalyst **1a** was

employed the R enantiomer was the major stereoisomer formed, whereas using catalyst **1b** afforded a greater proportion of the S enantiomer.

Table 3. Yields and optical activities obtained in the catalytic asymmetric ring-opening of epichlorohydrin by **2c**[a].

Substrate	Catalyst (10 mol%)	$AlCl_3$ (mol%)	Temp.	Time	Yield[b]	ee[c] (%)
2c	**1a**	-	RT	32d	-	-
2c	**1a**	10	RT	6d	61	30(R)
2c	**1b**	-	RT	3d	23	11(S)
2c	**1b**	10	RT	3d	60	18(S)

[a] reactions run in TBME.

[b]isolated yields after column chromatography based on **2c**.

[c]determined by chiral HPLC analysis. Major enantiomer in parentheses.

Conclusion

Reactions of all 3 salicylaldehydes **2a-c** with epichlorohydrin led to ring-opened products as a mixture of enantiomers. It is thought that this mixture arises from the lack of a single enantiomeric version of the attacking phenol group. For reactions which are particularly slow, it has been found that addition of alternative reagents which may be able to activate the phenolic group, such as $AlCl_3$, can dramatically increase the reaction rate and afford products in moderate to good enantiomeric excess. This procedure therefore opens a route for the preparation of certain α-aryloxy alcohols which may be difficult to synthesise using alternative methods.

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