Asymmetric Catalysis

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Asymmetric Counteranion-Directed Catalysis for the Epoxidation of Enals**

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Catalytic enantioselective epoxidation of olefins has traditionally defined the state of the art in asymmetric catalysis.[1] Groundbreaking achievements during the last thirty years include the Ti-catalyzed Sharpless epoxidation,[2] the Jacobsen epoxidation using manganese–salen complexes,[3] the polyamino acid-catalyzed Julia–Colonna epoxidation,[4] and the chiral ketone-catalyzed Shi epoxidation.[5] In addition, several other useful methods have been described.[6–9] Recently, equally elegant and useful organocatalytic asymmetric epoxidations of α,β-unsaturated aldehydes by iminium catalysis have been developed. Jørgensen and co-workers used a prolinol silyl ether catalyst in combination with hydrogen peroxide, while Lee and MacMillan later reported a procedure that required a hypervalent iodine reagent as the oxidant and a chiral imidazolidinone as the catalyst.[10] The potential exploitation of iminium catalytic epoxidation is enormous because of the ready availability of the required substrates[11] which lead to the synthesis of valuable chiral α,β-epoxy aldehydes that are then open for further manipulation,[1c,9a] However, the range of substrates is limited and only 1,2-disubstituted enals give an enantiomeric ratio of greater than 95:5, whereas trisubstitued enals give generally lower enantioselectivities.

We have recently developed asymmetric counteranion-directed catalysis (ACDC) as a new concept for enantioselective synthesis. Accordingly, catalytic reactions that proceed via cationic intermediates can be conducted in an asymmetric fashion if a chiral counteranion is incorporated into the catalyst. We originally used this approach to perform highly enantioselective organocatalytic conjugate reductions of α,β-unsaturated carbonyl compounds,[12] and subsequently extended it to transition-metal catalysis.[13] Herein we report initial results from using ACDC for the enantioselective organocatalytic epoxidation of α,β-unsaturated carbonyl compounds. We have identified a new catalytic salt **3m** that works well with disubstituted aromatic α,β-unsaturated aldehydes and gives excellent enantioselectivities with trisubstituted α,β-unsaturated aldehydes, which have previously been elusive substrates for any type of highly enantioselective epoxidation.

In our previous conjugate reduction system, the best catalyst was the morpholine salt of 3,3′-bis(2,4,6-triisopropylphenyl)-1,1′-binaphthyl-2,2′-diyl hydrogen phosphate (TRIP, **3a**),[12a] a phosphoric acid we have used in several different reactions.[14–16] This catalyst together with *tert*-butyl hydroperoxide (*t*BuOOH) as oxidant converted cinnamaldehyde (**1a**) into the desired 2,3-epoxyaldehyde **2a** in moderate yield, distereomeric ratio (d.r. 97:3), and enantiomeric ratio (e.r. 77:23; Table 1, entry 1). Other oxidants such as *m*CPBA, H_2O_2, and cumene hydroperoxide were also tested but gave inferior results. To further optimize the enantioselectivity of the reaction, a number of different amines were investigated. Of the amine salts studied (Table 1, entries 2–4), the dibenzylammonium salt of TRIP (**3d**) gave the best result (Table 1, entry 4, 95% yield, d.r. 98:2, e.r. 83:17). Dibenzylammonium salts with other phosphate counteranions gave significantly lower enantioselectivities (Table 1, entries 5 and 6). For further steric and electronic fine tuning, diverse dibenzyl amine derivatives were synthesized[17] and their TRIP salts (**3g–m**) tested (Table 1, entries 7–13). The epoxidation of cinnamaldehyde with catalyst **3m** (10 mol%) and *t*BuOOH (1.5 equiv) in dioxane gave **2a** in 71% yield, d.r. > 99:1, and e.r. 95:5 (Table 1, entry 13). Optimization of solvent and temperature resulted in slight improvement of both the yield and the e.r. value (Table 2, entry 1).

Having succeeded in developing an efficient and enantioselective catalyst (**3m**), we next examined the scope and limitation of our system for the epoxidation of various 1,2-disubstituted enals (Table 2). With aromatic substrates the epoxidation proceeds smoothly to furnish the desired products (**2a–n**) in good yields and excellent enantioselectivities (up to e.r. 98:2; Table 2, entries 1–13). In contrast to the iminium catalytic epoxidation reported by Jørgensen et al. which gave d.r. values between 90:10 and 98:2, [10a] by using our ACDC catalyst with aromatic substrates the diastereoselectivities are improved (d.r. values from 97:3 up to > 99:1). While simple alkyl-substituted enals are readily converted into the corresponding epoxide, the resulting stereoselectivity is slightly lower. For example, *trans*-2-nonenal (**1n**) gave the corresponding epoxide with a relatively high d.r. value (94:6) but moderate enantioselectivity (e.r. 85:15) as the major diastereoisomer. The minor *cis*-isomeric product was formed with an e.r. value of 96:4 (Table 2, entry 14).

β,β-Disubstituted α,β-unsaturated aldehydes such as 3-methylbut-2-enal (**1o**), gave the corresponding epoxide in only moderate enantioselectivity when using the system described by Jørgensen and co-workers.[10a] Pleasingly, we

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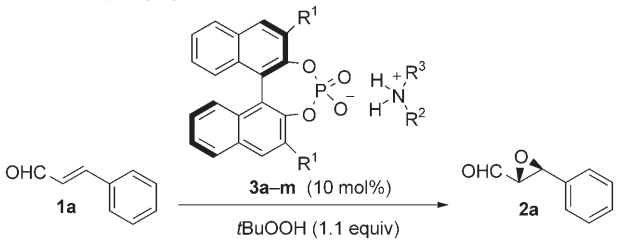
Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

Table 1: Development of an ACDC salt catalyst for the epoxidation of cinnamaldehyde (**1a**).[a]



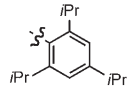
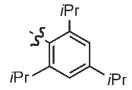
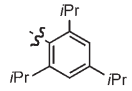
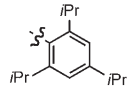
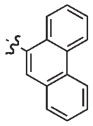
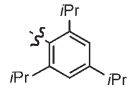
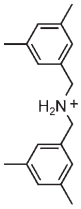
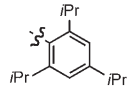
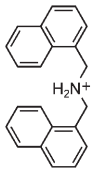
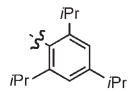
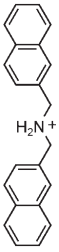
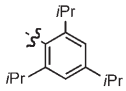
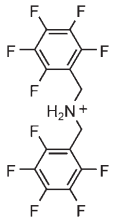
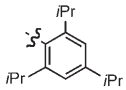
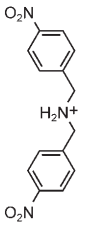
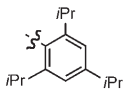
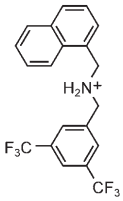
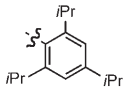
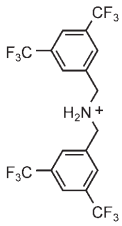
Entry	R^1	R^3, R^2	Cat.	Yield [%][b]	d.r.[c]	e.r.[d,e]
1			**3a**	40	93:7	77:23
2			**3b**	51	91:9	73:27
3			**3c**	85	95:5	78:22
4			**3d**	95	98:2	83:17
5			**3e**	75	98:2	62:38
6			**3f**	95	98:2	69:31
7			**3g**	63	98:2	79:21
8			**3h**	94	97:3	83:17
9			**3i**	87	95:5	80:20

Table 1: (Continued)

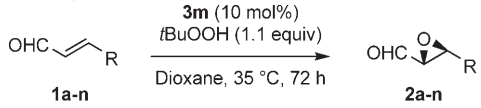
Entry	R^1	R^3, R^2	Cat.	Yield [%][b]	d.r.[c]	e.r.[d,e]
10			**3j**	55	96:4	86:14
11			**3k**	67	97:3	89:11
12			**3l**	85	98:2	91:9
13			**3m**	71	>99:1	95:5

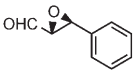
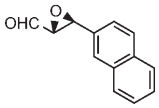
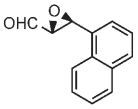
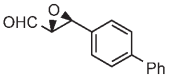
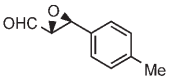
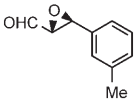
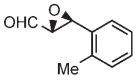
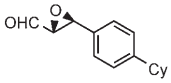
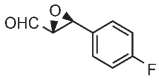
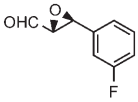
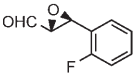
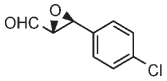
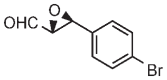
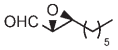
[a] Reaction performed on a 0.5-mmol scale with respect to cinnamaldehyde (**1a**) in dioxane (2 mL) at 50 °C for 24 h. [b] Yield of isolated products. [c] Determined by chiral GC. [d] Determined by chiral GC. [e] Absolute configuration [2*R*,3*S*] of **2a** was determined by comparison of its optical rotation with that reported.[9a,10a] Bn = benzyl.

found that our new ACDC catalyst **3m** in TBME (*tert*-butyl methyl ether) gave the desired product in 83% yield with an excellent enantioselectivity (e.r. 97:3; Table 3, entry 1). Similarly, aldehydes **1p** and **1q** gave the corresponding epoxides in good yields and very high enantioselectivities (Table 3, entries 2 and 3). We note that no other catalytic methodology has been developed for the oxidation of such trisubstituted enals. Upon epoxidation, citral (**1r**, as a 1:1 *E*/*Z* mixture) gave **2r** (the sex pheromone of the acarid mite)[18] under the optimized reaction conditions with an excellent yield and a 72:28 *trans*/*cis* ratio for the desired epoxide. A high e.r. value (96:4) was observed for the minor *cis* isomer while the major *trans* isomer was obtained with a moderate e.r. value (88:12) (Table 3, entry 4). As observed before in our Hantzsch ester mediated conjugate reductions, the outcome of this reaction was independent of the *E*/*Z* ratio of the substrate.[12a]

The high enantioselectivities observed with these trisubstituted substrates raises interesting mechanistic questions. In contrast to our previous ACDC enal reductions and the examples shown in Table 2, where the stereogenic center is created in the conjugate addition step, here the initial addition product (**B**) is achiral [Eq. (1). Only in the subse-

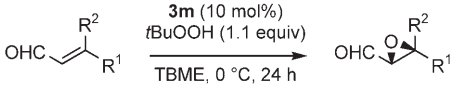
Table 2: ACDC epoxidation of α,β-unsaturated 1,2-disubstituted enals.[a]

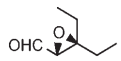
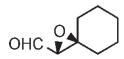
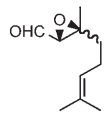


Entry	Product		Yield [%][b]	d.r.[c]	e.r.[d]
1		**2a**	75	>99:1	95.5:4.5
2		**2b**	76	>99:1	98:2
3[e]		**2c**	70	98:2	95.5:4.5
4[e]		**2d**	78	>99:1	95.5:4.5
5		**2e**	65	>99:1	96:4
6		**2f**	68	>99:1	96:4
7		**2g**	62	97:3	95.5:4.5
8		**2h**	60	>99:1	95:5
9		**2i**	78	>99:1	97:3
10		**2j**	82	>99:1	92:8
11		**2k**	69	98:2	95.5:4.5
12		**2l**	84	>99:1	93:7
13		**2m**	80	>99:1	93:7
14[f]		**2n**	67	94:6	85:15/96:4

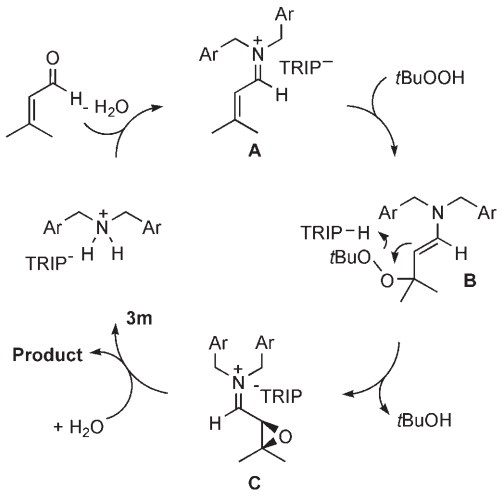
[a] Reactions were performed on a 0.5-mmol scale with respect to aldehyde in dioxane (2 mL) at 35 °C for 72 h. [b] Yield of isolated products. [c] Determined by chiral GC. [d] Determined by chiral GC. [e] After 120 h. [f] After 24 h in TBME at 0 °C. Cy = cyclohexyl:

Table 3: ACDC epoxidation of α,β-unsaturated 1,2,2-trisubstituted enals.[a]



Entry	Product		Yield [%][b]	e.r.[c]
1		**2o**	83	97:3
2		**2p**	85[d]	97:3
3		**2q**	75	95:5
4[e]		**2r**	95	72:28 d.r. 88:12 e.r. (*trans*) 96:4 e.r. (*cis*)

[a] Reactions were performed on a 0.5-mmol scale with respect to aldehyde in TBME (2 mL) at 0 °C for 12 h or 24 h for **1o** and **1p–r**, respectively. [b] Yield of isolated products. [c] Determined by chiral GC. [d] Determined by GC with internal standard. [e] At room temperature.



(1)

quent cyclization to iminium ion **C** is the stereogenic center created. Consequently, the chiral phosphate must be involved in this C–O bond-forming event. We propose the enantioselectivity results from a TRIP-assisted cyclization of intermediate **B**. This interesting enamine activation mode is novel and we are currently investigating other enamine catalytic reactions using salts of achiral amines with chiral Brønsted acids.

In summary, asymmetric counteranion-directed catalysis (ACDC) was successfully applied to the asymmetric epoxidation of α,β-unsaturated aldehydes to give high diastereo- and enantioselectivity. High enantioselectivity is also achieved with 1,2-disubstituted enals and β,β-disubstituted α,β-unsaturated aldehydes, thus implying a new mechanism for asymmetric enamine catalysis. Our research group is currently investigating the potential scope of this type of catalysis. Further studies on the application of ACDC to organocatalysis and other areas of chemistry will be reported in due course.

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