JOC *Note*

An *N*-Aryl-Substituted Oxazolidinone-Containing Ketone-Catalyzed Asymmetric Epoxidation with Hydrogen Peroxide as the Primary Oxidant

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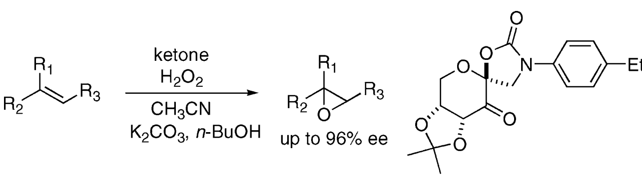

Asymmetric epoxidation of various olefins with an *N*-aryl-substituted oxazolidinone-containing ketone as catalyst and hydrogen peroxide as the primary oxidant has been investigated, and up to 96% ee was obtained.

Dioxiranes have proven to be valuable agents for the epoxidation of olefins.[1,2] Typically they are prepared by using a ketone and Oxone (potassium peroxymonosulfate). In our earlier studies on epoxidation with fructose-derived ketone **1**, we have shown that H_2O_2 coupled with a nitrile activator presents a viable alternative to Oxone for the formation of dioxiranes and subsequent epoxidation of olefins (Scheme 1).[3] High yields and ee values were obtained for a wide variety of trans- and trisubstituted olefins. Further studies have shown that some other ketones can be effective for the epoxidation with the RCN−H_2O_2 system.[4,5] In this epoxidation, peroxyimidic acid is likely the active oxidant for the formation of the dioxirane (Scheme 1).[6] Hydrogen peroxide (H_2O_2) is a highly desirable oxidant because of its high active oxygen content and its reduction product being water.[7−9] In addition, ketone-catalyzed epoxidation reactions with H_2O_2 require less solvent and salts than those with Oxone and do not require slow addition of oxidant.

Fructose-derived ketone **1** has been shown to be an effective catalyst for the epoxidation of a wide variety of trans- and trisubstituted olefins.[2b,c,10] During our further studies, we have found that oxazolidinone-containing ketones **2** gave high ee values for substrates such as *cis*-olefins,[11,12] styrenes,[11,13] and certain trisubstituted olefins[11,14] which are not effective with ketone **1**. The question is whether the RCN−H_2O_2 system can also be extended to epoxidation with ketone **2**. Herein, we wish to report our efforts on this subject.

Early on in the study it became apparent that ketone **2a** would not be useful under these conditions because of its rapid

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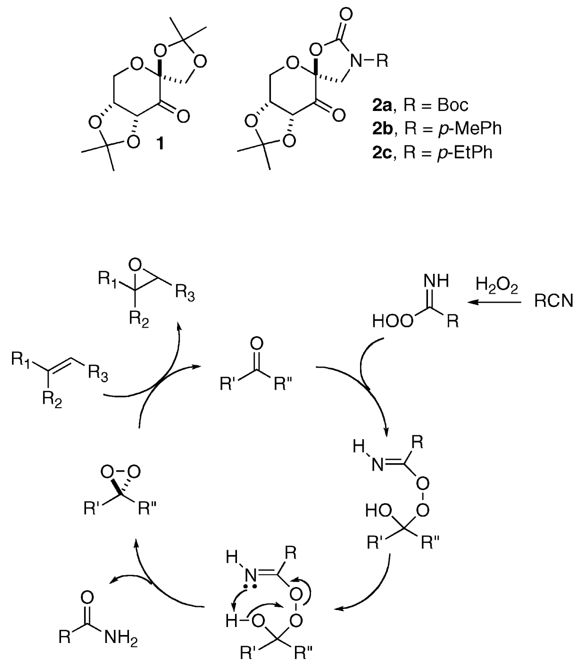
SCHEME 1



decomposition.[15] Ketones **2b**,**c** are more readily available than **2a** and appeared to be more robust under the reaction conditions so further study was conducted with these catalysts. Initial studies were carried out with *cis*-*β*-methylstyrene as a test substrate. Under the optimum conditions for ketone **1**, epoxidation with ketone **2b** using H_2O_2 in CH_3CN as solvent gave poor enantioselectivity (~50% ee). Subsequently, various solvents were tested for the epoxidation with 5 mol % ketone **2b**. As shown in Table 1, *n*-BuOH was found to be among the best solvents (Table 1, entry 11). The ee was increased to 78% when the amount of CH_3CN was reduced (Table 1, entry 12). After more optimization, it was found that 3.8 equiv of CH_3CN along with 3 equiv of H_2O_2 in *n*-BuOH−0.30 M aq K_2CO_3 in 4×10^{-4} M EDTA (1:1, v/v) gave the best results overall for a number of substrates.[16] In previous studies of various olefins, ketone **2c** often gave better overall results than **2b**,[13] so we decided to examine a variety of olefins with this catalyst (Table 2).[17] In many cases the ee values obtained are within a few percent of if not as high as the corresponding ee values with Oxone as oxidant. Up to 96% ee was obtained (Table 2, entry 7). The drop in enantioselectivity observed in some cases (e.g. Table 2, entry 11) is likely due to a solvent effect since the asymmetric induction of ketone **2** is largely attributed to electronic and/or hydrophobic effects which are solvent dependent.[11−14]

During the course of study it was also observed that the ketones are susceptible to decomposition under the reaction conditions. The reaction pH with 0.30 M K_2CO_3 is about 11.5, and at such a high pH α-deprotonation of the ketone occurs subsequently eliminating acetone.[18] It is also possible that the

(15) For facile hydrolysis of oxazolidinone with LiOOH see: Evans, D. A.; Britton, T. C.; Ellman, J. A. *Tetrahedron Lett.* **1987**, *28*, 6141.

(16) Under these conditions, 28% conversion and 78% ee were obtained for *cis*-*β*-methylstyrene with ketone **2a**.

(17) It was observed that olefins containing hydroxy groups are usually poor substrates under the reaction conditions for reasons that are not well understood.

(18) The formation of acetone can be detected by NMR.

TABLE 1. Asymmetric Epoxidation of *cis*-*β*-Methylstyrene with Ketone 2b[a]

		3 h		10 h	
entry	solvent	conv (%)[b]	ee (%)[b]	conv (%)[b]	ee (%)[b]
1	DME	28	68		
2	DMM	27	66		
3	DME/DMM (1:1)	28	65		
4	CH_2Cl_2	6	52		
5	CH_2Cl_2/EtOH (1:1)	54	57		
6	CH_2Cl_2/EtOH (2:1)	28	54		
7	MeOH			32	21
8	EtOH			67	47
9	*n*-PrOH			90	69
10	*i*-PrOH			92	70
11	***n*-BuOH**	**60**	**73**	**100**	**74**
12	***n*-BuOH**[c]			**87**	**78**
13	*t*-BuOH			97	74
14	*i*-$PrCH_2CH_2OH$			100	73
15	C_6H_6	13	69		
16	PhMe	13	68		
17	C_6H_6/EtOH (1:1)	37	68		
18	PhMe/EtOH (1:1)	14	69		
19	C_6H_6/*n*-BuOH (1:1)	47	71		
20	PhMe/*n*-BuOH	23	70		
21	C_6H_6/*n*-BuOH (1:6.5)	57	72		
22	dioxane[c]	35[d]	70		

[a] The reactions were carried out with olefin (0.5 mmol), ketone **2b** (0.025 mmol), and 30% H_2O_2 (0.20 mL, 2.0 mmol) in CH_3CN (0.20 mL, 3.8 mmol)−solvent (0.75 mL)−0.6 M K_2CO_3 in 4×10^{-4} M aqueous EDTA (0.75 mL) at 0 °C (bath temperature). [b] The conversions and ee values were determined by chiral GC (Chiraldex B-DM). [c] CH_3CN (0.10 mL, 1.9 mmol) used. [d] The reaction time is 4 h.

oxazolidinone is gradually hydrolyzed over time, presumably due to the nucleophilic action of peroxide anion.[15] The major consequence of this is that relatively unreactive olefins are difficult to drive to full conversion because the decomposition process(es) competes with the epoxidation process. However, for many substrates this system is a viable alternative to the Oxone protocol.

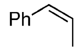
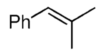
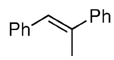
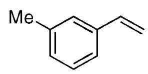
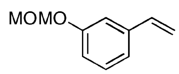
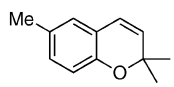
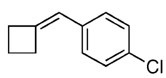
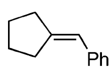
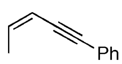
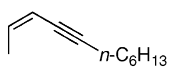
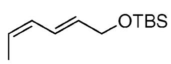
In summary, a method for asymmetric epoxidation with use of *N*-aryl oxazolidinone-containing ketones with H_2O_2 as primary oxidant has been described. A variety of olefins can be epoxidized with good yields and ee values. Use of H_2O_2 allows for use of less solvent, salts, and eliminates the need for slow addition of oxidant. The reactions are operationally simple, and in many cases give results similar to those obtained with Oxone.

Experimental Section

The general experimental information is similar to that recently described.[10b] Hydrogen peroxide (H_2O_2) is potentially explosive, and although no incidents occurred in our experience, care must be taken in handling this compound. In the epoxidation reaction, EDTA is used to minimize the decomposition of H_2O_2 catalyzed by any trace metals. Freshly purchased H_2O_2 from Aldrich was used in this study. It was found that vigorous stirring is crucial for epoxidation efficiency, particularly for less reactive substrates. All epoxides are known except Table 2, entries 5 and 8, and gave satisfactory spectroscopic characterization.

Representative Procedure for Asymmetric Epoxidation (Table 2, entry 2). A mixture of 2-methyl-1-phenyl-1-propene (0.135 g, 1.00 mmol) and ketone **2c**[21] (0.051 g, 0.15 mmol) in *n*-BuOH (3.0 mL) was cooled to 0 °C with an ice bath. CH_3CN (0.20 mL, 3.8 mmol) and 0.30 M K_2CO_3 in 4×10^{-4} M aqueous EDTA (3.0 mL) were then added, followed by H_2O_2 (30%, 0.30 mL, 3.0 mmol) with vigorous stirring at 0 °C. The mixture was stirred at 0 °C for

TABLE 2. Asymmetric Epoxidation of Olefins with Ketone 2c[a]

entry	substrate	catalyst loading (%)	time (h)	yield (conv)(%)	ee (%)	config.[b]
1		10	24	83 (99)[c]	82[d]	(-)(1R,2S)[11,19]
2		15	24	82 (96)[c]	92[d]	(+)[10b,11,20]
3		25	24	78 (90)[e]	88[f]	(+)(R,R)[10b,20]
4		25	24	93 (100)[c]	83[d]	(-)[13]
5		25	30	83 (94)[e]	80[f]	(-)
6		25	24	89 (100)[e]	91[f]	(+)[12c]
7		25	24	92 (93)[c]	96[d]	(+)(R)[14]
8		25	24	72 (100)[c]	90[d]	(+)
9		25	48	77 (91)[e]	88[f]	(-)(3R,4S)[11,12e]
10		30	48	65 (91)[c]	90[d]	(-)(2S,3R)[11,12e]
11		25	24	61 (100)[c]	82[d]	(-)[12d]

[a] The reactions were carried out with olefin (1.0 mmol), ketone **2c** (0.10−0.30 mmol), CH_3CN (0.20 mL, 3.8 mmol), *n*-BuOH (3.0 mL), aq 0.30 M K_2CO_3 in 4×10^{-4} M EDTA (3.0 mL), and 30% H_2O_2 (0.30 mL, 3.0 mmol) at 0 °C for the time indicated. [b] Absolute configuration was determined by comparing the measured optical rotations to the reported ones. [c] Conversion was determined by GC of the crude reaction mixture. [d] Enantioselectivity was determined by chiral GC (Chiraldex B-DM column). [e] Conversion was determined by ^{1}H NMR of the crude reaction mixture. [f] Enantioselectivity was determined by chiral HPLC (Chiralcel OD column).

24 h and was then poured into petroleum ether and extracted with petroleum ether. The combined organic layers were washed with water and saturated aqueous $Na_2S_2O_3$, dried (Na_2SO_4), filtered, concentrated, and purified by flash chromatography (silica gel was buffered with 1% Et_3N in petroleum ether; petroleum ether was used as eluent) to give 2,2-dimethyl-3-phenyloxirane as a colorless oil (0.121 g, 82% yield, 92% ee).

Table 2, entry 1: colorless oil; $[\alpha]^{25}_D$ −40.0 (*c* 0.77, $CHCl_3$) (82% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.28 (m, 5H), 4.07 (d, J = 4.4 Hz, 1H), 3.39−3.32 (m, 1H), 1.10 (d, J = 5.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.7, 128.2, 127.7, 126.8, 57.8, 55.4, 12.7.

Table 2, entry 2: colorless oil; $[\alpha]^{25}_D$ +38.3 (*c* 0.85, C_6H_6) (92% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.28 (m, 5H), 3.87 (s, 1H), 1.49 (s, 3H), 1.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 128.2, 127.6, 126.6, 64.8, 61.3, 25.0, 18.2.

Table 2, entry 3: colorless oil; $[\alpha]^{25}_D$ +99.3 (*c* 0.46, EtOH) (88% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50−7.30 (m, 10H), 3.98 (s, 1H), 1.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 136.1, 128.7, 128.4, 127.9, 127.7, 126.7, 125.4, 67.3, 63.3, 16.9.

Table 2, entry 4: colorless oil; $[\alpha]^{25}_D$ −17.3 (*c* 0.60, $CHCl_3$) (83% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28−7.23 (m, 1H), 7.14−7.08 (m, 3H), 3.84 (dd, J = 4.2, 2.8 Hz, 1H), 3.14 (dd, J = 5.6, 4.2 Hz, 1H), 2.81 (dd, J = 5.6, 2.8 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 137.7, 129.2, 128.6, 126.2, 122.9, 52.6, 51.4, 21.6.

Table 2, entry 5: colorless oil; $[\alpha]^{25}_D$ −13.8 (*c* 0.48, $CHCl_3$) (80% ee); IR (NaCl) 1587, 1152 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.24 (m, 1H), 7.01−6.92 (m, 3H), 5.18 (s, 2H), 3.84 (dd, J = 4.2, 2.8 Hz, 1H), 3.48 (s, 3H), 3.14 (dd, J = 5.6, 4.2 Hz, 1H),

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(21) Ketones **2b** and **2c** used in this study were prepared by the PDC oxidation of the alcohol precursors (for less reactive olefins, best results were obtained with freshly recrystallized ketones). It was observed that lower conversions were obtained with the ketone prepared from the TEMPO-bleach oxidation of the alcohol.[22] It appears that some residual impurities from TEMPO-bleach oxidation somehow affect the epoxidation.

(22) Zhao, M-X.; Goeddel, D.; Li, K.; Shi, Y. *Tetrahedron* **2006**, *62*, 8064.

2.79 (dd, J = 5.6, 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 139.6, 129.9, 119.2, 116.3, 113.4, 94.6, 56.3, 52.5, 51.4. Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.90; H, 6.94.

Table 2, entry 6: white solid; $[\alpha]^{25}_{D}$ +14.8 (c 1.80, $CHCl_3$) (91% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15−7.14 (m, 1H), 7.05−7.02 (m, 1H), 6.70 (d, J = 8.4 Hz, 1H), 3.86 (d, J = 4.2 Hz, 1H), 3.48 (d, J = 4.2 Hz, 1H), 2.29 (s, 3H), 1.57 (s, 3H), 1.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 131.0, 130.6, 130.2, 119.9, 118.0, 73.0, 63.1, 51.3, 25.9, 22.7, 20.7.

Table 2, entry 7: colorless oil; $[\alpha]^{25}_{D}$ +106.9 (c 1.38, $CHCl_3$) (96% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.31 (m, 2H), 7.13−7.10 (m, 2H), 3.83 (s, 1H), 2.67−2.57 (m, 1H), 2.51−2.36 (m, 2H), 1.99−1.83 (m, 2H), 1.76−1.60 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.5, 133.7, 128.6, 127.7, 66.9, 62.0, 31.5, 28.5, 12.6.

Table 2, entry 8: colorless oil; $[\alpha]^{25}_{D}$ +52.4 (c 0.67, $CHCl_3$) (90% ee); IR (NaCl) 1604, 1497, 1455 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.32 (m, 2H), 7.30−7.24 (m, 3H), 4.02 (s, 1H), 2.10−1.96 (m, 1H), 1.89−1.74 (m, 3H), 1.74−1.40 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4, 128.3, 127.7, 126.4, 72.8, 63.5, 34.2, 28.6, 25.5, 25.4. Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.56; H, 7.99.

Table 2, entry 9: colorless oil; $[\alpha]^{25}_{D}$ −34.8 (c 0.43, $CHCl_3$) (88% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48−7.45 (m, 2H), 7.35−7.30 (m, 3H), 3.65 (d, J = 4.4 Hz, 1H), 3.27 (qd, J = 5.2, 4.4 Hz, 1H), 1.51 (d, J = 5.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.1, 129.0, 128.6, 122.4, 85.5, 84.3, 54.7, 46.2, 15.1.

Table 2, entry 10: colorless oil; $[\alpha]^{25}_{D}$ −31.2 (c 0.41, $CHCl_3$) (90% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.42 (dt, J = 4.4, 1.6 Hz, 1H), 3.13 (qd, J = 5.2, 4.4 Hz, 1H), 2.22 (td, J = 7.2, 1.6 Hz, 2H), 1.53−1.47 (m, 2H), 1.42−1.22 (m, 8H), 1.40 (d, J = 5.2 Hz, 3H), 0.89 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 86.9, 75.1, 54.2, 46.1, 31.5, 28.7, 28.6, 22.8, 19.0, 14.9, 14.3.

Table 2, entry 11: colorless oil; $[\alpha]^{25}_{D}$ −19.1 (c 0.33, $CHCl_3$) (82% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.02 (dt, J = 15.4, 4.4 Hz, 1H), 5.60 (ddt, J = 15.4, 7.6, 1.7 Hz, 1H), 4.22 (dd, J = 4.4, 1.7 Hz, 2H), 3.43 (dd, J = 7.6, 4.0 Hz, 1H), 3.22 (quint., J = 5.4 Hz, 1H), 1.29 (d, J = 5.4 Hz, 3H), 0.91 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.3, 123.9, 63.2, 56.9, 54.7, 26.1, 18.6, 13.6, −5.1.

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Supporting Information Available: The data for the determination of the enantiomeric excess of the epoxides obtained with ketone **2c** along with the ^{1}H and ^{13}C NMR spectra of epoxides. This material is available free of charge via the Internet at http://pubs.acs.org.

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