A Catalytic Cycle for the Asymmetric Synthesis of Epoxides Using Sulfur Ylides

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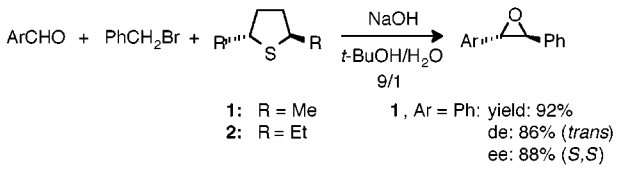
Since the pioneering work[1] of Furukawa in the late 1980s, some examples[2] of nonracemic epoxidation have been reported using aromatic aldehydes and chiral sulfur ylides. Enantiopure oxiranes are versatile compounds for organic synthesis. They can be transformed[3] into 1,2-difunctionalized derivatives by nucleophilic ring opening reactions. Our group has recently developed[4] an efficient asymmetric conversion of aldehydes into epoxides via a simple C_2 symmetric sulfide, (2*R*,5*R*)-2,5-dimethylthiolane **1**. We reported that trans epoxides could be obtained with high yields (87%-92%) and enantiomeric excesses (86−96%) in a one-pot synthesis employing mild reaction conditions and a stoichiometric amount of sulfide (Scheme 1).

In addition, the feasibility of a catalytic process was demonstrated. The use of 0.1 equiv of sulfide **1** led to an excellent yield and ee, but the reaction time at room-temperature had to be prolonged to one month! We now wish to present[5] the results of a new study devoted to (i) reducing the reaction time while maintaining the yields and enantiomeric excesses, (ii) applying these conditions to a variety of aromatic aldehydes, and (iii) demonstrating greater chiral control by using both enantiomers of **1** and a new chiral sulfide, (2*R*,5*R*)-2,5-diethylthiolane **2**.

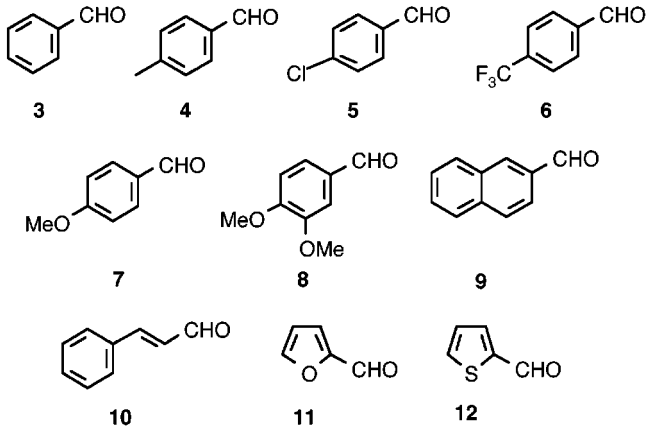
Scheme 1



Results and Discussion

During the development of the asymmetric conversion of aldehydes into oxiranes, our group (and probably others) has observed that the overall process tends to be sluggish when one introduces bulky groups in the initial sulfide. A preliminary study[4b] of the reaction mechanism led us to believe that there are two slow steps in the epoxidation: formation of the sulfonium salt and addition of the ylide to the carbonyl compound. In contrast, deprotonation of the sulfonium salt and ring closure of the betaine are much faster. As the second slow step determines the enantioselectivity, we wished to accelerate the first one. We now report a simple way to achieve this acceleration along with an optimization of the reactant concentrations and the reaction temperature.

Scheme 2



We have expanded the scope of the epoxidation to include the aldehydes **6**,**7**,**9**−**12** (Scheme 2). The results of the epoxidations are summarized in Table 1. Under our standard noncatalytic conditions, 4-methoxybenzaldehyde **7** was converted in 80% yield with 88% ee (Table 1, entry 15) despite the acid sensitivity of the resulting epoxide. Similar results were obtained with 2-naphthaldehyde **9** (entry 17) and a vinyl-oxirane was obtained from cinnamaldehyde **10** in 93% yield and 87% ee (entry 20).

The epoxidation of heteroaromatic aldehydes has proved problematic. While no epoxidation was reported using camphor-derived sulfonium ylides,[2j] examples of this type of reaction were recently reported.[2n,6] In our hands the reaction of 2-furaldehyde **11** and 2-thienylaldehyde **12** proceeded nicely at ambient temperature with good conversion and enantioselectivities (93 and 89%, entries 23 and 24). However, one has to be very careful during the isolation of the resulting oxiranes which exhibit great acidic sensitivity.

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Table 1. Asymmetric Synthesis of Various Oxiranes

entry	aldehyde	thiolane R =	iodide salt	sulfide (equiv)	time (days)	yield (%)[a]	de (trans) (%)[b]	ee (*S*,*S*) (%)[c]
1	**3**	Me (2*R*,5*R*)	-	1	2	92[d]	86	88
2			*n*-Bu_4NI	0.1	4	82	85	85
3			*n*-Bu_4NI	0.2	2	80	80	85
4			NaI	0.1	5	74	80	89
5		Me (2*S*,5*S*)	*n*-Bu_4NI	0.2	6	95	80	80 (*R*,*R*)
6		Et (2*R*,5*R*)	-	1	4	97	88	93
7			*n*-Bu_4NI	0.1	6	90	85	92
8	**4**	Me (2*R*,5*R*)	-	1	2	88[d]	84	88
9		Et (2*R*,5*R*)	-	1	4	95	85	89
10			*n*-Bu_4NI	0.1	6	79	88	88
11	**5**	Me (2*R*,5*R*)	-	1	2	89[d]	84	86
12			*n*-Bu_4NI	0.1	6	77	80	72
13		Et (2*R*,5*R*)	-	1	4	88	86	89
14	**6**	Et (2*R*,5*R*)	*n*-Bu_4NI	0.1	6	82	85	90
15	**7**	Me (2*R*,5*R*)	-	1	2	80	82	88
16	**8**	Et (2*R*,5*R*)	*n*-Bu_4NI	0.1	6	33[e]	85	86
17	**9**	Me (2*R*,5*R*)	-	1	2	88	84	86
18			*n*-Bu_4NI	0.1	5	75	80	64
19		Et (2*R*,5*R*)	-	1	4	88	84	86
20	**10**	Me (2*R*,5*R*)	-	1	2	93	95	87
21			*n*-Bu_4NI	0.1	6	60	78	69
22			NaI	0.1	6	70	80	86
23	**11**	Me (2*R*,5*R*)	-	1	4	89	80	93
24	**12**	Me (2*R*,5*R*)	-	1	4	90	81	89
25			*n*-Bu_4NI	0.1	6	75	75	80

[a] Yield after purification on a silica gel column. [b] Diastereoisomeric excess determined on the ^1H NMR of the crude product. [c] Enantiomeric excess determined by chiral HPLC using a Daicel AD column. [d] Our previous work.[4b] [e] Unstable product on silica gel.

In some cases we have endeavored to increase enantioselectivities by using new thiolanes. We began with the slighly bulkier and less volatile (2*R*,5*R*)-2,5-diethylthiolane **2** which was prepared in 94% yield from (3*S*,6*S*)-3,6-octanediol[7] using the procedure[4] developed for the synthesis of the dimethyl-substituted analogue **1**. Increased enantioselectivities were indeed achieved with **2**. (*S*,*S*)-Stilbene oxide was obtained in 93% ee (entry 6), showing a gain of 5% as compared to the dimethylthiolane **1** mediated reaction (entry 1). Three other examples (tolualdehyde **4**, 4-chlorobenzaldehyde **5**, and 2-naphthaldehyde **9**) led to similar selectivities (entries 9, 13, and 19).

We have then developed a practical *catalytic* cycle, for which very few examples have been reported.[2e,j,l,8] In our procedure the formation of the sulfonium salt is effected by commercially available benzyl bromide, thereby avoiding silver salts, triflates, or diazoalkanes. It should be noted that under standard conditions, chlorides are not electrophilic enough and that benzyl iodide is usually not available with acceptable purity. We hoped to activate the benzyl bromide through the addition of an iodide salt leading to a metathetical halogen exchange and in situ formation of benzyl iodide. In the racemic series with thiolane itself, several iodide salts (NaI, Me_4NI, *n*-Bu_4NI) were tested and indeed showed an acceleration with the shortest reaction times recorded for *n*-Bu_4NI. Activation of the reaction was similarly observed using nonracemic catalytic conditions with thiolane **1**.

Reaction conditions were optimized with respect to reactant concentrations and temperature. Three experiments were carried out with 0.1 equiv of chiral sulfide **1** and benzaldehyde in concentrations of 0.25, 0.5, and 1 M (Table 2). With 0.5 M aldehyde (entry 2), the reaction time was reduced to 4 days, with preservation of yield, de, and ee values. With 1 M aldehyde (entry 3), the yield of stilbene oxide dropped by approximately 40%. It is possible that a higher concentration favors side processes such as the Cannizzaro reaction.[9] We then examined the effect of temperature with a 0.5 M concentration of aldehyde. At 35 °C or 50 °C the reaction proceeded smoothly (73 and 70% yields) with shorter reaction times, but caused a significant decrease of the ee (76 and 74%, respectively, as compared to 85% at rt).

Table 2. Asymmetric Synthesis of Stilbene Oxide with Various Concentrations of Aldehyde

entry	[PhCHO] (M)	time (days)	yield (%)[a]	de (trans) (%)[b]	ee (*S*,*S*) (%)[c]
1	0.25	21	80	86	81
2	0.5	4	82	85	85
3	1	5	41	82	89

[a] Yield after purification on a silica gel column. [b] Diastereoisomeric excess determined on the ^1H NMR of the crude product. [c] Enantiomeric excess determined by chiral HPLC using a Daicel AD column.

These studies led us to the following optimized catalytic epoxidation conditions at room temperature (Scheme 3): benzaldehyde (1 equiv, 0.5 M), benzyl bromide (2 equiv), *n*-Bu_4NI (1 equiv), NaOH (2 equiv) and the chiral sulfide (0.1 equiv) in a mixture of 9/1 *t*-BuOH/H_2O. In the case of stilbene oxide (entry 2, Table 1), after 4 days, 82% of oxirane was isolated with good ee and de values (85%, 85%). If the amount of sulfide was increased to 0.2 equiv, the reaction could be achieved in only 2 days with conservation of yield and selectivity (entry 3, Table 1).

For a generalized asymmetric synthesis, both enantiomers of the target molecule must be accessible. We have demonstrated that this is true for our method by prepar-

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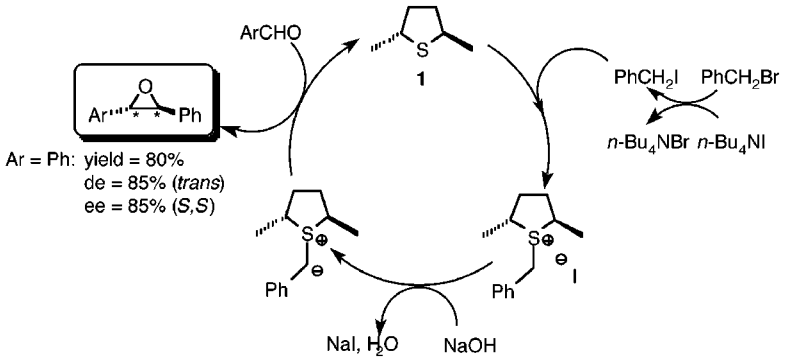
Scheme 3



ing the (2*S*,5*S*) enantiomer of **1**. (2*R*,5*R*)-Hexanediol can be purchased commercially and is also available[10] by lipase resolution[10a−c] of the meso + DL mixture of hexanediols. Formation of the dimesylate of (2*R*,5*R*)-hexanediol and nucleophilic displacement[4a,11] with Na_2S provided the previously unreported (2*S*,5*S*)-2,5-dimethylthiolane in good yield (93%). This enantiomer was used successfully for the synthesis of *trans*-(*R*,*R*)-stilbene oxide (entry 5, Table 1).

The catalytic reaction conditions were extended to various aromatic aldehydes using the three chiral sulfides (Table 1). Chiral control was exerted by both enantiomers of thiolane **1** with oxiranes isolated in good to excellent yields (60−95%) after 4 to 6 days (entries 12, 18, 21, 25). Four examples (entries 7, 10, 14, 16) were investigated with a catalytic amount of (2*R*,5*R*)-2,5-diethylthiolane **2**. For stilbene oxide the highest ee for the catalytic series was attained: 92%, with 90% yield (entry 7). Diastereomeric induction was generally good (up to 95%), but we observed some decrease from the stoichiometric to the catalytic series. The largest variation was observed with cinnamaldehyde (entries 20, 21). A recent study by Aggarwal and co-workers[12] on the diastereoselectivity of the reaction of sulfur ylides with aldehydes proposed that the formation of anti betaines (leading to trans oxiranes) is irreversible. On the other hand, they reported that the formation of syn betaines is reversible and can lead to mixtures of cis and trans oxiranes. Consequently, slower reactions will favor reversibility and lead to a higher proportion of trans epoxides. In contrast, here, we have observed cases for which the slower catalytic reactions led to a lower diastereoselection. To explain this, other factors must be considered, including the effect of salts.[13] We have also observed variations[2l] of the ee values with some aldehydes between the catalytic and stoichiometric series (small with benzaldehyde and tolualdehyde, 14−22% with others). In this case, the nature of the iodide salt is important: if NaI was used instead of *n*-Bu_4NI (sets of entries 1, 2, 4 and 20, 21, 22) ee variations were not observed.

In conclusion we have developed a new catalytic approach to optically actives oxiranes via a chiral sulfonium ylide. We have found simple, practical and cheap conditions under which epoxides can be obtained using 0.2 or 0.1 equiv of sulfide. Anhydrous solvents, inert atmosphere, strong bases, low temperature, preformation of sulfonium salts or use of phenyldiazomethane are not required. We have reported the straightforward synthesis of both enantiomers of dimethylthiolane **1** and their use as chirality inductors. From 0.1 equiv of sulfide, in one pot, trans oxiranes were obtained with good yields and enantiomeric excesses, after a reasonable reaction time (4 to 6 days). Moreover, diethylthiolane **2** is a very promising new chiral sulfide (ee up to 93%). A variety of aromatic aldehydes were converted using both sulfides. These results provide a complementary route to chiral oxiranes directly from readily available aldehydes, thereby avoiding the Wittig synthesis and subsequent oxidation of an intermediate alkene.[14]

Experimental Section

Chromatographic purification of compounds was achieved with Merck 60 silica gel (40−63 μm). Thin-layer chromatography (TLC) was used routinely to monitor the progress of epoxidation reactions. ^{1}H NMR spectra were recorded using at 250 MHz. Data appear in the following order: chemical shifts in ppm, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant *J* in Hz, number of protons. ^{13}C NMR spectra were acquired at 62.9 MHz with the same spectrometer, operating with broad band ^{1}H decoupling. TMS is the internal standard for the $CDCl_3$ solutions. Mass spectra were obtained in EI mode at 70 eV. Specific optical rotations (given in 10^{-1} deg cm^2 g^{-1}) were measured at 589 nm. Mps stand uncorrected. High-pressure liquid chromatography (HPLC) was performed with a diode array detector and a Daicel AD chiral column 250 × 4.6 mm (length × i.d.) with *n*-hexane/isopropyl alcohol 90/10 at a flow rate of 1 mL/min as the eluant.

Typical Procedure. Synthesis of 2-(4-Chlorophenyl)-3-phenyloxirane. To a solution of (2*R*,5*R*)-2,5-dimethylthiolane (0.05 mmol, 250 μL of a 0.2 M solution of dimethylthiolane in *t*-BuOH/H_2O 9/1, 0.1 equiv) in 750 μL of a mixture of *t*-BuOH/H_2O 9/1 were added benzyl bromide (120 μL, 1 mmol, 2 equiv), powdered NaOH (40 mg, 1 mmol, 2 equiv), tetrabutylammonium iodide (185 mg, 0.5 mmol, 1 equiv), and the 4-chlorobenzaldehyde (72 mg, 0.5 mmol, 1 equiv). The reaction mixture was stirred at room temperature. The reaction was judged complete by thin-

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layer chromatography (TLC). TLC plates were visualized by UV light and by treatment with a solution of 2,4-DNPH (400 mg in 100 mL of HCl 1 N). Water (5 mL) was added. The aqueous phase was extracted with diethyl ether (10 mL, 3 times), and the combined organic layers were dried over $MgSO_4$ and then concentrated to dryness. The crude product was subjected to column chromatography (silica gel, 98/2 petroleum ether/diethyl ether) to afford the oxirane (88 mg, 0.385 mmol, 77% yield, de: 80%, ee: 72%). Trans isomer: ^{1}H NMR δ: 7.26−7.39 (m, 9H), 3.80 and 3.82 (AB syst, J = 1.7, 2H); ^{13}C NMR δ: 136.7, 135.6, 134.1, 128.7, 128.6, 128.5, 126.8, 125.4, 62.9, 62.1. Anal. Calcd: C: 72.89, H: 4.81, O: 6,506.94. Found: C: 73.12, H: 4.90, O: 7.04. HPLC: cis: 4.9 and 5.0 [(*R*,*S*) and (*S*,*R*) enantiomers could not be completely separated], trans (UV maximum absorption: 232 nm): 5.8 and 10.6 min [(*R*,*R*) and (*S*,*S*) enantiomers].

(2*R*,5*R*)-2,5-Diethylthiolane 2. A solution of (3*S*,6*S*)-octane-3,6-diol (1 g, 6.84 mmol) and triethylamine (2.3 mL, 16.4 mmol) in dichloromethane (15 mL) was cooled at −18 °C. Methanesulfonyl chloride (1.23 mL, 15 mmol) was added dropwise while the temperature was maintained between −20 °C and −15 °C. After addition, the mixture was warmed to 0 °C. A 1 N HCl solution (4 mL) was added. The extraction was carried out with dichloromethane (15 mL, three times). The organic layer was separated, washed with a saturated $NaHCO_3$ aqueous solution (10 mL), and dried over $MgSO_4$. After filtration and evaporation of the solvent, a colorless oil of (1*S*,4*S*)-4-methanesulfonyloxy-1-ethylhexyl methanesulfonate (2.05 g, quantitative yield) was obtained. ^{1}H NMR δ: 4.70−4.75 (m, 2H), 3.03 (s, 6H), 1.81−1.84 (m, 4H), 1.70−1.78 (m, 4H), 0.99 (t, J = 7.4, 6H); ^{13}C NMR δ: 84.3, 39.1, 29.2, 27.9, 9.7. Sodium sulfide nonahydrate (3.4 g, 14 mmol) was added to a solution of the preceding dimesylate in ethanol (20 mL). The mixture was stirred at room temperature for 15 days. A milky suspension of sodium methanesulfonate was formed. It was poured into water (15 mL) and extracted with pentane (4 mL, 4 times). The combined organic phase was washed with brine and dried over $MgSO_4$. After filtration, pentane was evaporated with the evaporator water bath being kept at 0 °C to avoid any loss of the volatile thiolane. A pale yellow liquid with an unpleasant odor (700 mg, 4.85 mmol, 71% yield) was obtained. It appeared unnecessary to further purify (2*R*,5*R*)-2,5-diethylthiolane. ^{1}H NMR δ: 3.25−3.40 (m, 2H), 2.15−2.20 (m, 2H), 1.48−1.70 (m, 6H), 0.95 (t, J = 7.3, 6H); ^{13}C NMR δ: 51.4, 36.9, 30.7, 13.4; EIMS m/z (%) = 144 (16) [M^+], 115 (100) [M^+-C2H5], 81 (37), 69 (29), 59 (31), 55 (38), 41 (69); HRMS: found 144.1017, requires 144.0973; $[\alpha]^{23}_D$ = +164° (c = 1.27, $CHCl_3$).

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Supporting Information Available: Chromatographic separations and spectral data of oxiranes. The material is available free of charge via the Internet at http://pubs.acs.org.

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