diacetic acid was a minor product(4%)(entry No. 13).

The spectral data of *para*-phenylenediacetic acid are as follows; ^{1}H-nmr(DMSO-d_6): δ(ppm) 3.50(s, 4H, 2CH$_2$-), 7.15 (s, 4H, Ar). ^{13}C-nmr(DMSO-d_6): δ(ppm) 20.78(-CH$_2$-), 122.41 ($\geq$C-H), 147.88($\geq$C-), 168.79($\geq$C=O). MS(m/e); 194. Ir (KBr) ν_{CO}; 1700cm^{-1}. m.p.; 248-250°C. On the other hand, the spectral data of *para*-tolylacetic acid are as follows; ^{1}H -nmr(CDCl$_3$): δ(ppm) 2.30(s, 3H, CH$_3$), 3.50(s, 2H, CH$_2$), 7.10(s, 4H, Ar). Ir(KBr): ν_{CO}; 1700cm^{-1}. m.p.; 89-90°C. These results match those from literature[8]. According to the mechanism proposed by Alper and Abbayes[9], the iron pentacarbonyl is reacted with a hydroxide ion transferred from aqueous layer to organic layer by the phase transfer catalyst to give the tetracarbonylferrate anion, and xylylene dihalide is oxidatively added to the anion. Successively, carbon monoxide may be inserted into alkyl-metal bond to give acyl-metal complex. Finally, alkylacylmetal complex by attack of hydroxide ion gave the carboxylic acid and acylmetal complex, true catalyst, was regenerated.

Carbon monoxide was slowly bubbled for 30 minutes through the stirred solution of 2M-KOH(10 m*l*)-dichloromethane(10 m*l*) and dibenzo-18-crown-6-ether(0.3 mmol) or quaternary ammonium salt(0.6 mmol). A solution of metal complex(0.25 mmol) in 3-5 m*l* of dichloromethane was added and then the reaction mixture was vigorously stirred at room temperature for 1 hr. Xylylene dihalide(2.5 mmol) in 3-5 m*l* of dichloromethane was added and stirring was continued with carbon monoxide bubbled for 20 hrs. The phases were

carefully separated; the aqueous layer was washed with two 10 m*l* of ether, acidified(conc. HCl), and then extracted with four 15 m*l* of ether. The combined ether extracts were washed with a 20 m*l* of water, dried with magnesium sulfate and evaporated to give the crude products, that were purified by using vacuum sublimation apparatus.

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Enantioselective Reduction of Racemic Three-Membered Heterocyclic Compounds. 2. Reaction of Epoxides and Episulfides with (-)-Diisopinocampheylborane in the Presence of Lithium Chloride[1]

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In the previous paper[2], we reported that the optically-active (-)-diisopinocampheylborane[(-)-IPC$_2$BH]-lithium chloride (1:0.1) system reduced enantioselectively racemic 1,2-epoxybutane to give optically-active R-(-)-2-butanol in around 22% ee at 0°C or-20°C. We interpreted this result as the chiral IPC$_2$BH coordinates preferentially on R-1,2-epoxybutane rather than on S-1,2-epoxybutane in an approximate ratio of 3:2 and then the *in situ* formed lithium diisopinocampheylchloroborohydride attacks the epoxy ring of the adduct to give the alcohol product[2,3].

This new methodology seems to be promising for resolution of racemic three-membered heterocyclic compounds. Consequently, it appeared desirable to explore the applicability of this system to other structurally-different epoxides and another class of this series, episulfides.

Results and Discussion

The reaction mixture involves 2 equiv of racemate and 1 equiv of IPC$_2$BH-LiCl (1:0.1). Therefore, only 1 equiv of racemate is coordinated enantioselectively with 1 equiv of IPC$_2$BH, and only the coordinated compound is then reduced by the *in situ* formed IPC$_2$B$^\ominus$ClH species.

We applied this system for the resolution of three racemic aliphatic epoxides such as 1,2-epoxybutane, 1,2-epoxyoctane, and 3,3-dimethyl-1,2-epoxybutane and a racemic aromatic one such as styrene oxide at 0°C, the result of which are summarized in Table 1.

As shown in Table 1, all the epoxides examined were readily reduced to the corresponding alcohols within 3 h at 0°C to provide yields of 79-86%. Racemic 1,2-epoxybutane is

Communications to the Editor

Bull. Korean Chem. Soc., Vol. 9, No. 1, 1988 63

Table 1. Reaction of Racemic Epoxides with the (−)-Diisopinocampheylborane^a-Lithium Chloride (1:0.1) System in Tetrahydrofuran at 0°C

Epoxide	Product	Yield (%)	$[\alpha]_D^{22}$(neat)	% ee[b]	Absolute configuration[b]
1,2-Epoxybutane	2-Butanol[c]	79	3.17	23.5	R
	2-Butanol[d]	80	+3.12	23.1	S
1,2-Epoxyoctane	2-Octanol[c]	85	-3.02	30.5	R
	2-Octanol[b]	86	+2.95	29.8	S
3,3-Dimethyl-1,2-epoxybutane	3,3-Dimethyl-2-butanol[c]	81	-2.04	25.2	R
Styrene oxide	1-Phenyl-ethanol[c]	85	-2.36	5.5	S

[a]Prepared with 92% ee (+)-α-pinene, $[\alpha]_D^{22}$ +47.1°. [b]Based on the maximum values reported: R-(-)-2-butanol[4], $[\alpha]_D^{25}$ -13.5°; S-(+)-2-octanol[5], $[\alpha]_D^{20}$ +9.9°; R-(-)-3,3-dimethyl-2-butanol[6], $[\alpha]_D^{20}$ -8.1°; R-(+)-1-phenylethanol[7], $[\alpha]_D^{20}$ +42.85°. [c]From the reduction with the (-)-IPC₂BH-LiCl (1:0.1) system. [d]From the reduction of distillate of the unreacted epoxide with LiAlH₄.

Table 2. Reaction of Racemic Episulfides with the (−)-Diisopinocampheylborane^a-Lithium Chloride (1:0.1) System in Tetrahydrofuran at 0°C

Episulfide	Product	Yield (%)	$[\alpha]_D^{22}$(neat)	% ee[b]	Absolute configuration[b]
1-Butene sulfide	2-Butanethiol[c]	74	-3.04	17.7	R
Styrene sulfide	1-Phenyl-ethanethiol[c]	72	-6.05	6.2	S

[a]and [c]See corresponding footnotes in Table 1. [b]Based on the maximum values reported: (R)-2-butanethiol[8] -17.15°; (S)-2-butanethiol[9] +15.7°, (S)-1-phenylethanethiol[10] -89.0° (c = 6, EtOH).

resolved and reduced to give (R)-(-)-2-butanol in 23.5% ee. The treatment of remaining 1 equiv of 1,2-epoxybutane by lithium aluminum hydride provides 2-butanol in 23.1% ee with the opposite configuration of S. Increasing the chain length shows significant effect [(R)-(-)-2-octanol obtained in 30.5% ee]. However, introduction of two alkyl substituents has little effect [(R)-(-)-3,3-dimethyl-2-butanol, 25.2% ee]. All the aliphatic epoxides examined provide alcohols consistently enriched in the R enantiomer. An aromatic epoxide, styrene oxide gives 1-phenylethanol in 5.5% ee with the opposite configuration of S with levorotation.

In the case of episulfides, 1-butene sulfide (an aliphatics) and styrene sulfide (an aromatics) were examined, and the results are summarized in Table 2. The system readily reduces episulfides to the corresponding thiols in yields of 72-74% within 3 h at 0°C.

The system resolves racemic 1-butene sulfide to give 2-butanethiol in 17.7% ee with the same configuration to the case of aliphatic epoxides, (R)-(-). In the case of aromatic episulfide, styrene sulfide, the enantioselectivity is also decreased to 6.2% ee. The configuration of 1-phenylet-

hanethiol, however, is S with levorotation.

Conclusion

The chiral (-)-diisopinocampheylborane-lithium chloride (1:0.1) system resolved racemic epoxides examined in the range of 5.5-30.5% ee and racemic episulfides examined in the range of 6.2-17.7% ee. This enantioselectivity assumes to be the result from the enantioselective coordination of IPC₂BH to the heteroatom of racemic three-membered cyclic compounds. In addition to that, it is clearly evident from the discussion that all of the alcohols and thiols obtained from the reaction of epoxides and episulfides with this chiral borane-lithium chloride system [from (+)-α-pinene] are consistently enriched in the enantiomer with levorotation. There seems not to be a sharp correlation between the steric requirement of the compounds examined and the observed % ee, however we can anticipate that the steric requirement of chiral organoborans introduced might play a major role on the enantioselective coordination and thus the enantioselective reduction. This extensive study is under way.

Experimental Section

All glasswares used in this study were dried thoroughly in a dried oven for at least 3 h at 150°C and all operations were carried out under anhydrous nitrogen atmosphere. The experimental techniques used in handling air-sensitive materials are described elsewhere[11]. α-Pinene was treated with LiAlH₄ just before use. Epoxides and episulfides used are either commercial products of the highest purity or products synthesized according to the literature[12]. The alcohol and thiol products were further purified through preparative GLC using 10% Carbowax 20M on Chromosob P column (6 ft. × 0.5 in.). Quantitative analysis of the reduction products was performed on a Hewlett-Packard Model 5790A GLC equipped with a flame ionization detector. The optical rotation was measured by a DIP-360 Digital Automatic Polarimeter (Jasco).

Asymmetric Reduction of Epoxides with (−)-Diisopinocampheylborane-Lithium Chloride (1:0.1). The procedure for the reaction of 1,2-epoxyoctane is representative. An oven-dried 100-m*l* flask, equipped with a septum inlet and a bent adaptor which is connected to a mercury bubbler, was charged with 0.21 g of predried lithium chloride (5 mmol). The flask was further dried with flame while flushing the system with dry nitrogen. After cooling the flask to 0°C with an ice-water bath under a positive nitrogen pressure, the flask was charged with 5 m*l* of 10 M BH₃·SMe₂ (50 mmol), and 15.6g (115 mmol, 15% excess) of (+)-α-pinene (Aldrich, $[\alpha]_D^{22}$ +47.1°, 92% ee) in 15 m*l* of THF was added dropwise with constant stirring. After stirring for 3 h at 0°C, the flask was stored at 0°C for 3 days. The flask was then immersed in an ice-water bath and 10 m*l* of 10.0 M solution of 1,2-epoxyoctane (100 mmol) was poured into the flask as rapidly as possible with vigorous stirring. The precipitate of IPC₂BH was disappeared in 0.5 h. The reaction mixture was stirred for an additional 3 h at 0°C and then allowed to warm to room temperature. Excess α-pinene and unreacted epoxide were collected by distillation. All the remaining volatile material was then removed by evaporation *in vacuo*, and to this oily residue was added 100

m*l* of ether. The mixture was then hydrolyzed with water, followed by oxidation with alkaline hydrogen peroxide in the usual manner[11]. The mixture was saturated with potassium carbonate and the separated organic layer after drying with anhydrous magnesium sulfate was subjected to fractional distillation. The yield of crude 2-octanol was 85% (5.5g). The product was further purified through 10% CW 20M column and the purity of reduction product was confirmed by an analytical GLC. The optical rotation of 2-octanol was $[\alpha]_D^{22}$ $-3.02°$ (neat), 30.5% ee in R^5.

The collected portion of 1,2-epoxyoctane was reduced to 2-octanol with excess $LiAlH_4$ at $0°C$, and then the mixture was treated with 1.5 m*l* of 10 M $BH_3 \cdot SMe_2$ to hydroborate excess α-pinene. The mixture was then hydrolyzed, followed by oxidation with alkaline hydrogen peroxide. The separated alcohol product was purified as described above to give a pure 2-octanol $[\alpha]_D^{22}$ $+2.95°$ (neat), 29.8% ee in S^5.

Asymmetric Reduction of Episulfides with (−)-Di-isopinocampheylborane-Lithium Chloride (1:0.1). The procedure for the reaction of episulfides with this system is exactly same as the case of reaction of epoxides described above. In the case of 1-butene sulfide, the optical rotation of the pure reduction product (2-butanethiol) was $[\alpha]_D^{22}$ $-3.04°$ (neat), 17.7% ee in R^8.

Acknowledgement. The authors in Yeungnam University wish to acknowledge the financial support by Korea Science and Engineering Foundation.

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An Electrochemical Study on the Formation and Growth of Conducting Polyaniline

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In 1862 Letheby[1] reported that a dark green precipitate could be obtained on a platinum electrode when aniline was electrochemically oxidized in aqueous sulfuric acid solutions. Subsequent investigators[2-5] verified this result and called the precipitate "aniline black", and attempted a larger scale oxidation until about 1950. Mohilner, Adams, and Argersinger[6] proposed a reaction scheme, on the basis of polarization curves, which seems to be generally accepted at the present time. They suggested that the oxidation process proceeds via head-to-tail coupling of the cation radical of aniline. An ESR spectrum that has given ample evidence for cation radical intermediates, was reported(4) in an aprotic solvent. However, it was not observed in aqueous solution. Adams group[4] proposed in the case of N-substituted anilines that a dication intermediate undergoes nucleophilic attack by the parent amine and results in the tail-to-tail coupling.

Under certain conditions the peak currents in the cyclic voltammograms were observed to be increasing with the number of cycles. In view of recent studies on conducting polymers[7-12], it is interesting to note that these increases may be interpreted as an evidence for polymer growth of conducting character.

In this communication electrochemically measured data are presented on the formation and growth of conducting polyaniline. The data were obtained from cyclic voltammetry and kinetic measurements of electrochemical oxidation of aniline on platinum electrodes in aqueous sulfuric acid solutions. The potentials given here are referred to a saturated calomel electrode(SCE).

Figure 1 illustrates typical cyclic voltammograms(CVs) for the growth of polianiline(PANI) films on the platinum electrode in aqueous 1.0M H_2SO_4 solution. From about 0.85V *vs* SCE in the first scan, an anodic rising current associated with the oxidation of aniline is observed. However,