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Stereochemistry of Ring-Opening Reactions of Epoxide with Aluminum and Zinc Porphyrins. Relation to the Mechanism of Ring-Opening Polymerization

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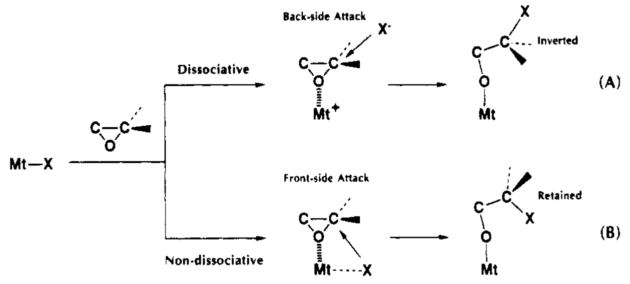
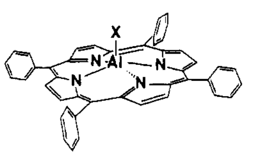
ABSTRACT: Ring-opening reactions of 2,3-epoxybutanes with aluminum 5,10,15,20-tetraphenylporphine ((TPP)AlX (**1**; X = SPr, OMe)) and zinc 5,10,15,20-tetraphenyl-21-methylporphine ((NMTPP)ZnX (**2**; X = SPr, OMe)) were carried out in the presence of protic compounds such as 1-propanethiol (PrSH) and methanol (MeOH), where the *cis*- and *trans*-epoxides were converted to *threo*- and *erythro*-3-substituted 2-butanols, respectively. When the polymers of *cis*- and *trans*-2,3-epoxybutanes, prepared by the polymerizations with (TPP)AlCl, were cleaved with pentylsodium, *dl*- and *meso*-butanediols were obtained, respectively, as the diol fragments. Thus, the ring-opening reactions of 2,3-epoxybutanes with **1** and **2** both proceed with inversion of the configuration at the carbon atom of the epoxide ring where cleaved.

Introduction

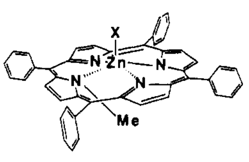
It has been established that anionic ring-opening reactions of epoxides mostly proceed with inversion of the configuration at the carbon atom of the epoxide ring where cleaved, for which a linear transition state mechanism involving a dissociated nucleophilic species has been proposed (Scheme IA).[1] Inversion of the configuration has also been demonstrated in the ring-opening polymerization of epoxides with anionic, coordinate anionic, and cationic initiators such as *tert*-BuOK, Et_3Al/H_2O, Et_2Zn/H_2O, and $BF_3{\cdot}OEt_2$.[2] On the other hand, some limited examples of stereochemically retentive ring-opening reactions of epoxides have been reported.[3] A representative example is given by the reaction of 2,3-epoxybutane with $AlCl_3$ giving 3-chloro-2-butanol, where the *cis*- and *trans*-epoxides are converted to the *erythro*- and *threo*-chlorohydrins, respectively, in more than 90% stereoselectivities in nitromethane at a low temperature such as −10 °C.[3a] In this case, a nondissociated four-centered mechanism as illustrated in Scheme IB has been postulated.

Scheme I



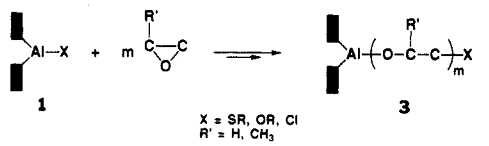


(TPP)AlX (**1**)
1a X = Cl
1b X = Me
1c X = SPr
1d X = OMe

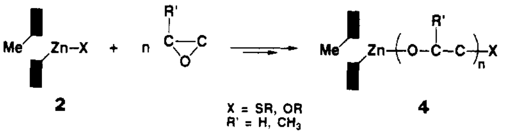


(NMTPP)ZnX (**2**)
2a X = Et
2b X = SPr
2c X = OMe

In the present study, the stereochemistry of ring-opening reactions of *cis*- and *trans*-2,3-epoxybutanes (BO) with aluminum porphyrins ((TPP)AlX **1**) and zinc N-substituted porphyrins ((NMTPP)ZnX, **2**) was examined. These two metalloporphyrins serve as excellent initiators for the polymerization of epoxides such as epoxyethane and 1,2-epoxypropane, which proceeds via (porphinato)metal alcoholates (**3** and **4**) as the growing species (eqs 1 and 2).[4,5] We have so far demonstrated that these polymerizations exhibit the following characteristic features: (i) various substituted epoxides such as 1,2-epoxypropane as well as nonsubstituted epoxide (epoxyethane) can be polymerized with living character to give the polymers of uniform, controlled molecular weights;[6] (ii) **1** allows the formation of poly(1,2-epoxypropane) rich in isotactic sequences;[7] (iii) with aluminum porphyrin as initiator, the rate of polymerization and the tacticity of the produced polymer are significantly affected by the structure of the porphyrin ligand;[8] (iv) with **1** as initiator, the copolymerization of *cis*- and *trans*-2,3-epoxybutanes results in a preferred consumption of the sterically less hindered cis isomer to the trans isomer[9] (coordinate anionic character of polymerization); (v) with **2** as initiator, both initiation and propagation steps can be accelerated upon photoexcitation of the porphyrin ring with visible light.[5] In sharp contrast, with anionic initiators such as alkali-metal alcoholates, the polymerization of substituted epoxides is generally accompanied by chain-transfer reactions by the participation of the substituents. Furthermore, the polymerization of 1,2-epoxypropane with alkali-metal alcoholates gives virtually atactic polymer. Thus, the features i–v observed for the polymerizations via **3** and **4** (eqs 1 and 2) strongly indicate the participation of nondissociated metal alcoholate growing species in the chain-growing steps. Therefore, in these cases, the configuration of epoxide is expected to be retained when a concerted mechanism (Scheme II) analogous to Scheme IB is operative.



(1)



(2)

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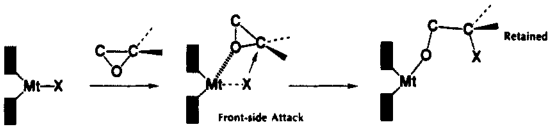
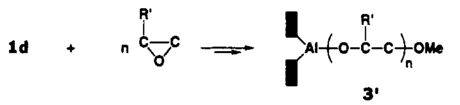
Scheme II



For the ring-opening reaction of 2,3-epoxybutanes with (TPP)AlX (1) and (NMTPP)ZnX (2), the method of *immortal* polymerization was applied. The concept of *immortal* polymerization has been established in the polymerization of epoxides initiated with (TPP)AlX (1) in the presence of a protic compound such as MeOH, which gives polyethers of uniform molecular weights.[10] In this case, MeOH rapidly exchanges with the growing alcoholate species (**3**) to generate (TPP)AlOMe (**1d**) (eq 3), and

(3)

3 **1d**



(4)

3'

X = SR, OR, Cl
R' = H, CH$_3$

the subsequent reinitiation of the polymerization by **1d** (eq 4) and the exchange reactions similar to eq 3 follow. The number of the polymer molecules is equal to the sum of those of 1 and MeOH, and the molecular weight of the polymer can be controlled by changing the initial mole ratio $[\text{epoxide}]_0/([\mathbf{1}]_0 + [\text{MeOH}]_0)$. Therefore, when an excess amount of MeOH with respect to epoxide is added in the presence of **1**, the one-to-one adduct between MeOH and epoxide is expected to be formed catalytically as for **1** without formation of the polymeric products. The polymerization of epoxides with (NMTPP)ZnX (**2**) in the presence of a protic compound also proceeds with *immortal* character,[5] and the same methodology was applied to the ring-opening reaction of epoxide with **2**.

Experimental Section

Materials. 5,10,15,20-Tetraphenylporphine (TPPH$_2$) was synthesized from pyrrole and benzaldehyde in propionic acid and recrystallized from CHCl$_3$/MeOH.[11] 5,10,15,20-Tetraphenyl-21-methylporphine (NMTPPH) was synthesized by the reaction of TPPH$_2$ with methyl iodide in CHCl$_3$ containing 7.5% acetic acid in a sealed tube at 65–70 °C for 7 days.[5,12] The crude reaction mixture was chromatographed on silica gel using CH$_2$Cl$_2$/CHCl$_3$ as eluent followed by basic alumina using CH$_2$Cl$_2$/*n*-hexane as eluent, and a bright green band collected was subjected to recrystallization from CHCl$_3$/MeOH to give NMTPPH as purple crystals. Trimethylaluminum (Me$_3$Al), chlorodiethylaluminum (ClEt$_2$Al), and diethylzinc (Et$_2$Zn) were fractionally distilled in a nitrogen atmosphere under reduced pressure. Benzene (C$_6$H$_6$) and benzene-*d*$_6$ (C$_6$D$_6$) were refluxed over a sodium wire and distilled in a nitrogen atmosphere. CH$_2$Cl$_2$, washed successively with concentrated H$_2$SO$_4$, water, and aqueous NaHCO$_3$ and dried over anhydrous CaCl$_2$, was distilled over CaH$_2$ in a nitrogen atmosphere. CDCl$_3$ was distilled after refluxing over CaH$_2$ under nitrogen. 1-Propanethiol (PrSH) was distilled over anhydrous CaSO$_4$ under nitrogen. Methanol (MeOH) was distilled over magnesium treated with iodine under nitrogen. *cis*-2,3-Epoxy- and *trans*-2,3-epoxybutanes (2,3-butene oxide, BO), obtained from Aldrich or prepared respectively from *cis*- and *trans*-2-butenes upon treatment with *N*-bromosuccinimide[13] followed by ring closure of the resulting bromohydrins in concentrated aqueous KOH,[14] were stirred with a mixture of KOH pellets and CaH$_2$ and subjected to valve-to-valve distillation in a nitrogen atmosphere. *dl*-2,3-Butanediol and *meso*-2,3-butanediol were prepared respectively by hydration of *cis*- and *trans*-2,3-epoxybutanes in the presence of perchloric acid.[14] *threo*-3-(Propylthio)- and *erythro*-3-(propylthio)-2-butanols were prepared respectively by reacting *cis*- and *trans*-2,3-epoxybutanes with sodium 1-propanethiolate, which was prepared from PrSH and sodium ethoxide in absolute ethanol.[15] *threo*-3-Methoxy- and *erythro*-3-methoxy-2-butanols were obtained respectively by reacting *cis*- and *trans*-2,3-epoxybutanes with MeOH in the presence of H$_2$SO$_4$.[16] Pentylsodium was prepared by adding 1-chloropentane to a dispersion of sodium metal in dry *o*-xylene containing 1% oleinic acid under nitrogen.[17]

Procedures. Preparation of (TPP)AlCl (1a). A 100-mL round-bottomed flask equipped with a three-way stopcock, containing TPPH$_2$ (1 mmol) and a Teflon-coated magnetic stirring bar, was purged with dry nitrogen, and CH$_2$Cl$_2$ (20 mL) and ClEt$_2$Al (0.125 mL, 1.2 equiv) were successively added to the flask by means of a hypodermic syringe in a nitrogen stream. The mixture was stirred at room temperature for 2 h in a nitrogen atmosphere, and then the volatile fractions were removed from the reaction mixture under reduced pressure at room temperature to leave (TPP)AlCl (**1a**) as a purple powder.[18]

Preparation of the (TPP)AlSPr (1c)/PrSH System. To a 20-mL round-bottomed flask containing TPPH$_2$ (0.1 mmol) under nitrogen were successively added C$_6$H$_6$ (4 mL) and Me$_3$Al (0.012 mL, 1.2 equiv) by means of a hypodermic syringe in a nitrogen stream, and the mixture was stirred at room temperature for 2 h in a nitrogen atmosphere. Then, the volatile fractions were removed from the reaction mixture under reduced pressure at room temperature to leave (TPP)AlMe (**1b**) as a purple powder.[19] To this flask was added C$_6$H$_6$ (2 mL) to dissolve **1b**, followed by 50 equiv of PrSH in a nitrogen stream. The mixture was stirred overnight at room temperature under irradiation with visible light (xenon arc light, $\lambda > 420$ nm), where the bluish purple solution gradually turned to reddish brown characteristic of the formation of **1c**.[20]

Preparation of the (TPP)AlOMe (1d)/MeOH System. To a 50-mL round-bottomed flask containing **1b** (0.4 mmol) were added CH$_2$Cl$_2$ (8 mL) and MeOH (4 mL) in a nitrogen stream, and the mixture was stirred at room temperature. After 2 days, the volatile fractions were removed from the reaction mixture under reduced pressure at room temperature to leave (TPP)AlOMe (**1d**) as a reddish purple powder,[21] to which were then added CH$_2$Cl$_2$ (4 mL) and 50 equiv of MeOH with respect to **1d**.

Preparation of (NMTPP)ZnSPr (2b) and the 2b/PrSH System. To a 20-mL round-bottomed flask, wrapped in aluminum foil and equipped with a three-way stopcock, containing NMTPPH (0.2 mmol) under nitrogen was added a C$_6$H$_6$ solution (4 mL) of Et$_2$Zn (0.3 mmol) by means of a hypodermic syringe in a nitrogen stream. After stirring magnetically for 1.5 h at room temperature in the dark, the volatile fractions were removed from the reaction mixture under reduced pressure to leave (NMTPP)ZnEt (**2a**) as a purple powder.[22] To this flask, wrapped in aluminum foil, was added C$_6$H$_6$ (8 mL) to dissolve **2a**, followed by 3.3 equiv of PrSH in a nitrogen stream. After the mixture was stirred overnight at room temperature in the dark, the volatile fractions were removed from the reaction mixture under reduced pressure at room temperature, and the residue was heated at 90 °C for 2 h under reduced pressure to leave (NMTPP)ZnSPr (**2b**) as a deep green powder.[23] For the preparation of the **2b**/PrSH system, C$_6$H$_6$ (4 mL) and 50 equiv of PrSH with respect to **2b** were added to this flask.

Preparation of the (NMTPP)ZnOMe (2c)/MeOH System. To a 20-mL round-bottomed flask wrapped in aluminum foil, containing a benzene solution (8 mL) of **2a** (0.2 mmol) under nitrogen, was added 50 equiv of MeOH, and the reaction mixture obtained after stirring magnetically at 60 °C for 24 h in the dark was used for the ring-opening reaction of epoxides.

Ring-Opening Reaction of 2,3-Epoxybutanes (BO). A typical example of the ring-opening reaction of 2,3-epoxybutanes (BO) is as follows. To a 20-mL round-bottomed flask fitted with a three-way stopcock, containing a benzene solution (2 mL) of (NMTPP)ZnSPr (**2b**) (0.1 mmol) and PrSH (5 mmol) under nitrogen, was added *cis*-2,3-epoxybutane (*cis*-BO) (2.5 mmol) through the three-way stopcock by means of a hypodermic syringe in a nitrogen stream, and the reaction mixture was stirred at 35 °C. For the reaction under irradiation with visible light, the mixture was illuminated with a 300-W (ILC Technology Model LX-300F) or 500-W (Ushio UXL-500) xenon arc lamp from a distance of 35 cm through a glass filter (Kenko type L42, Kenko Co., Ltd.) to cut out light of wavelength shorter than 420 nm. For the reaction in the dark, the flask was wrapped in aluminum foil. The reaction at 80 °C was carried out in a sealed NMR tube (5 mm ϕ). To determine the yield and stereochemistry of the products, aliquots of the reaction mixture were periodically taken out from the flask by using a syringe in a nitrogen stream and subjected to ^{1}H NMR and GC analyses. A capillary column OV-101 was used at the column temperature of 120 °C for GC analysis of the reaction mixture of BO with (TPP)AlSPr (**1c**) or (NMTPP)-ZnSPr (**2b**), while that with (TPP)AlOMe (**1d**) or (NMTPP)-ZnOMe (**2c**) was analyzed by using a capillary column PEG 20M (column temperature, 100 °C).

Synthesis of Poly(2,3-epoxybutanes) for Cleavage Reaction. To a 50-mL round-bottomed flask fitted with a three-way stopcock, containing a CH_2Cl_2 solution (4 mL) of (TPP)AlCl (**1a**, about 0.2 mmol) under nitrogen, was added 200 equiv of *cis*- or *trans*-2,3-epoxybutane (BO) through the three-way stopcock by a syringe in a nitrogen stream, and the mixture was stirred magnetically at room temperature. After a definite time, the reaction mixture was evaporated to dryness under reduced pressure at room temperature, and the residue dissolved in $CHCl_3$ was added to a large volume of MeOH, affording the polymer as a slightly colored precipitate. The yields of the polymers of *cis*- and *trans*-BO were 48 and 43%, respectively.

Cleavage of Poly(2,3-epoxybutanes) with Pentylsodium. To a stainless-steel autoclave containing poly(2,3-epoxybutane) (0.5–0.7 g) were successively added *n*-heptane (14 mL/0.1 g of polymer) and a dispersion of pentylsodium (1.2 M, 3.4 mL/0.1 g of polymer), and the mixture was allowed to react at 90 °C in a nitrogen atmosphere. After 43 h, the reaction mixture was cooled to room temperature, and anhydrous ethanol (10 mL) was added to quench the reaction. The mixture was poured into ethanol (58 mL/0.1 g of polymer) cooled in an ice–water bath, and concentrated hydrochloric acid was added to adjust the pH value of the system to 7–9. After the mixture was centrifuged to remove the insoluble materials, the resulting supernatant solution was deionized by agitating with ethanol–wet Amberlite MB-1 ion exchange resin (28.8 mL/0.1 g of polymer). After 1 h, the resin was removed by filtration, and the solvent was stripped off under reduced pressure with an aspirator at room temperature, and then the residue was subjected to extractions with isopropyl ether, MeOH, and $CHCl_3$, successively. The organic layers thus obtained were combined, filtered, and evaporated at room temperature with an aspirator, and the residue was distilled under reduced pressure to give 2,3-butanediol, which was almost pure as observed by GC and ^{1}H NMR. The yields of the diol fractions from the polymers of *cis*- and *trans*-2,3-epoxybutanes were 11.8 and 10.2%, respectively.

Measurements. For the estimation of M_n and M_w/M_n of polymers, gel permeation chromatography (GPC) was performed at 40 °C using tetrahydrofuran as eluent with a flow rate of 1.0 mL·min^{-1}. The molecular weight calibration curve was obtained by using standard polystyrenes; 2 890 000 ($M_w/M_n = 1.09$), 422 000 (1.04), 107 000 (1.07), 43 900 (1.01), 16 700 (1.02), 9000 (1.06), 6200 (1.04), 4000 (1.10), and 2800 (1.05). ^{1}H and ^{13}C NMR measurements were performed in C_6D_6 or $CDCl_3$ using a JEOL type GSX-270 spectrometer, where the chemical shifts were determined with respect to C_6H_6 (δ 7.40) or $CHCl_3$ (δ 7.28) for ^{1}H NMR and $CDCl_3$ (δ 77.1) for ^{13}C NMR. Gas chromatographic analyses were performed on an Ohkura gas chromatograph Model 103 equipped with a capillary column (OV-101 (25 m) or PEG 20M (30 m)) and a flame ionization detector.

Results

Ring-Opening Reactions (Polymerizations) of 2,3-Epoxybutanes (BO) with Aluminum Porphyrin ((TPP)AlCl (1a)) and Zinc *N*-Methylporphyrin ((NMTPP)ZnSPr (2b)). Similar to epoxyethane and 1,2-epoxypropane, 2,3-epoxybutanes were found to react with (TPP)AlCl (**1a**) to give the corresponding aluminum alcoholate species. For example, in the ^{1}H NMR spectrum in $CDCl_3$ of the reaction mixture of *cis*-2,3-epoxybutane (*cis*-BO) with **1a** ($[cis\text{-BO}]_0/[\mathbf{1a}]_0 = 10$), four signals characteristic of the aluminum alcoholate species, (TPP)-AlO–CH[a](CH_3[b])CH[c](CH_3[d])–, were observed in the upfield region at δ –2.3 (a), –1.8 (b), –0.9 (c), and –1.2 (d).[24] Integration of these signals and that due to the pyrrole β protons of the (TPP)Al moiety (8 H) indicated the quantiative formation of the alcoholate species. When 200 equiv of *cis*-2,3-epoxybutane were added to a CH_2Cl_2 solution of **1a** at 35 °C, the polymerization took place to attain 74% conversion in 16 h, where the produced polymer showed a unimodal but relatively broad GPC chromatogram, from which M_n and M_w/M_n were estimated based on polystyrene standards to be 10 400 and 1.74, respectively. The observed M_n value is very close to the expected one by assuming the formation of one polymer molecule from every molecule of the initiator (10 700), again indicating the quantitative formation of the growing alcoholate species from **1a**. The ^{13}C NMR spectrum in $CDCl_3$ of the oligomer, isolated by column chromatography from the reaction mixture ($[cis\text{-BO}]_0/[\mathbf{1a}]_0 = 10$, 100% conversion), showed a signal at δ 58, which is assignable to the terminal methine carbon attached to a chlorine atom.[25] All the above observations demonstrate that the polymerization of *cis*-2,3-epoxybutane with (TPP)AlCl (**1a**) proceeds according to eq 1. Under similar conditions, the polymerization of the trans isomer initiated with **1a** also occurred but much more slowly than that of the cis isomer.

In the ^{1}H NMR spectrum of a mixture of *cis*-2,3-epoxybutane with (NMTPP)ZnSPr (**2b**) ($[cis\text{-BO}]_0/[\mathbf{2b}]_0 = 50$) in C_6D_6 at 30 °C, the signals of the SPr group of **2b** (δ –0.8 (SCH_2), –0.45 (CH_2), and 0.1 (CH_3)) completely disappeared after irradiation with visible light for 1.5 h, while new signals assignable to the zinc alcoholate species, (NMTPP)Zn–OCH(CH_3[a])CH(CH_3[b])–, appeared at δ –1.21 (a) and –0.48 (b).[26] On the other hand, in the dark, no reaction took place throughout the NMR observation for 11 days. Thus, similar to the case of 1,2-epoxypropane, the ring-opening reaction of 2,3-epoxybutanes with **2b** takes place under irradiation with visible light, giving the zinc alcoholate species.

Stereochemistry of the Ring-Opening Reaction of 2,3-Epoxybutanes (BO) with (TPP)AlX (1). On the basis of the above observation that (TPP)Al alcoholates are formed by the reaction between 2,3-epoxybutanes (BO) and (TPP)AlX (**1**), the stereochemistry of the ring-opening reaction of BO with **1** was investigated by employing the methodology of *immortal* polymerization using the systems (TPP)AlSPr (**1c**)/PrSH and (TPP)AlOMe (**1d**)/MeOH, and the results are summarized in Table I.

The ring-opening reaction of *cis*-2,3-epoxybutane (*cis*-BO) with **1c** in the presence of PrSH ($[cis\text{-BO}]_0/[\text{PrSH}]_0/[\mathbf{1c}]_0 = 25/49/1$) proceeded at room temperature (~20 °C) in C_6H_6 under irradiation with visible light (xenon arc light, $\lambda > 420$ nm) (run 1). Figure 1 shows the ^{1}H NMR spectrum of the reaction mixture after 9 days, where the signals due to *cis*-BO were not observed at δ 2.9 and 1.2, indicating the complete consumption of the epoxide. The signals a′–d′ are due to PrSH added in excess with respect to the epoxide. A set of the signals a–h is assigned to the reaction product, which is unambiguously the threo isomer of 3-(propylthio)-2-butanol by reference to the authentic sample.[15] No signals characteristic of the erythro isomer (e.g., δ 3.91 (C*H*OH))[15] were detected. The absence of the erythro isomer in the product was also confirmed by GC analysis. Together with the fact that no signals due to the polymeric oxy-2,3-dimethylethylene units were detected, the above NMR profiles indicate the quantitative for-

Table I
Ring-Opening Reactions of 2,3-Epoxybutanes (BO) with (TPP)AlX (1) and Protic Compounds (HX)

run	X	BO	$[BO]_0/[HX]_0/[1]_0$	light	temp, °C	time, day	3-X-2-butanol conv,[a] %	3-X-2-butanol confign[a,b]
1[c]	SPr	cis	25/49/1	irradn[f]	rt[g]	9	100	threo
2[c]	SPr	trans	25/49/1	irradn[f]	rt[g]	11	22	erythro
3[d]	SPr	cis	1/2/0	irradn[f]	35	30	0	
4[d]	SPr	trans	1/2/0	diffuse light	rt[g]	15	0	
5[e]	OMe	cis	25/50/1	dark	rt[g]	11	15	threo
6[e]	OMe	trans	25/50/1	dark	rt[g]	11	36	erythro

[a] ^1H NMR. [b] GC. [c] In C_6H_6 (flask). [d] In C_6D_6 (5-mm-ϕ NMR tube). [e] In CH_2Cl_2 (flask). [f] 500-W xenon arc light ($\lambda > 420$ nm). [g] Room temp (~20 °C).

Table II
Ring-Opening Reactions of 2,3-Epoxybutanes (BO) with (NMTPP)ZnX (2) and Protic Compounds (HX)

run	X	BO	$[BO]_0/[HX]_0/[2]_0$	light	temp, °C	time, day	3-X-2-butanol conv,[a] %	3-X-2-butanol confign[a,b]
1[c]	SPr	cis	25/50/1	irradn[e]	35	11	>95	threo
2[c]	SPr	trans	50/100/1	irradn[e]	35	11	17	erythro
3[c]	SPr	cis	0.5/0/1	irradn[e]	35	19	64	threo
4[c]	SPr	trans	0.5/0/1	irradn[e]	35	19	52	erythro
5[c]	OMe	cis	25/49/1	irradn[e]	35	33	3	threo
6[c]	OMe	trans	25/49/1	irradn[e]	35	58[f]	17	erythro
7[d]	OMe	trans	25/49/1	dark	80	1	43	erythro
8[d]	OMe	cis	1/2/0	irradn[e]	35	30	0	
9[d]	OMe	trans	1/2/0	irradn[e]	35	12	0	
10[d]	OMe	trans	1/2/0	dark	80	11	0	

[a] ^1H NMR. [b] GC. [c] In C_6H_6 (flask). [d] In C_6D_6 (5-mm-ϕ NMR tube). [e] 300-W xenon arc light ($\lambda > 420$ nm). [f] 11 days under irradiation plus 47 days in the dark.

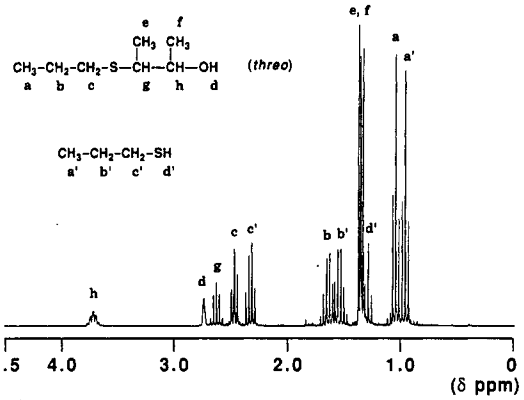


Figure 1. Reaction of *cis*-2,3-epoxybutane (*cis*-BO) with (TPP)-AlSPr (**1c**) in the presence of 1-propanethiol (PrSH) in C_6H_6 at room temperature (~20 °C) under irradiation with xenon arc light ($\lambda > 420$ nm) for 9 days ($[cis\text{-BO}]_0/[PrSH]_0/[\mathbf{1c}]_0 = 25/49/1$). ^1H NMR spectrum in C_6D_6 (C_6H_6 (δ 7.4) as internal standard) of the reaction mixture (run 1 in Table I).

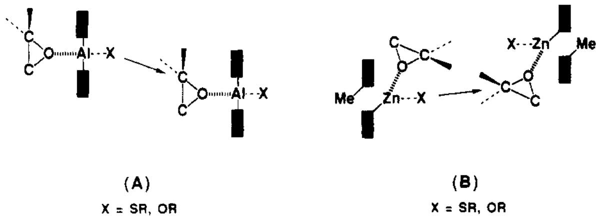
mation of *threo*-3-(propylthio)-2-butanol from *cis*-2,3-epoxybutane by reaction with (TPP)AlSPr (**1c**) in the presence of PrSH. The reaction of the *trans*-epoxide was carried out under the same conditions, where *erythro*-3-(propylthio)-2-butanol was formed as the sole product in 22% yield in 11 days (run 2). It should be also noted that in the absence of (TPP)AlSPr (**1c**) 2,3-epoxybutanes remained unreacted with PrSH under the same conditions (runs 3 and 4). In the reactions with (TPP)AlOMe (**1d**) in the presence of MeOH under similar conditions ($[BO]_0/[MeOH]_0/[\mathbf{1d}]_0 = 25/50/1$, ~20 °C in CH_2Cl_2 in the dark), *cis*- and *trans*-2,3-epoxybutanes were converted to *threo*- and *erythro*-3-methoxy-2-butanols, respectively, without formation of the polymeric products (runs 5 and 6).

Thus, the ring-opening reactions of 2,3-epoxybutanes with the aluminum thiolate and alcoholate species of aluminum porphyrins (**1**) both proceed with inversion of the configuration at the carbon atom of the epoxide ring where cleaved.

In order to establish the stereochemistry of the ring-opening polymerization of epoxides initiated with aluminum porphyrins (**1**), the polymers of *cis*- and *trans*-2,3-epoxybutanes, prepared with (TPP)AlCl (**1a**) as initiator, were cleaved by the action of pentylsodium according to the method reported by Vandenberg,[2b] and the 2,3-butanediol fragments were isolated and analyzed by ^1H NMR and GC. By reference to the authentic samples,[14] the product from poly(*cis*-2,3-epoxybutane) was identified as *dl*-2,3-butanediol, while that from poly(*trans*-2,3-epoxybutane) was identified as the meso isomer. Thus, inversion of the configuration is also the case for the ring-opening polymerization of 2,3-epoxybutanes via a (porphinato)aluminum alcoholate (**3**) as the growing species (eq 1).

Stereochemistry of the Ring-Opening Reaction of 2,3-Epoxybutanes (BO) with (NMTPP)ZnX (2). Ring-opening reactions of *cis*- and *trans*-2,3-epoxybutanes (BO) with (NMTPP)ZnX (**2**; X = SPr (**2b**), OMe (**2c**)) were similarly carried out in the presence of the corresponding protic compounds in C_6H_6 at 35 °C under irradiation with visible light (xenon arc light, $\lambda > 420$ nm), and the results are summarized in Table II. When *cis*-2,3-epoxybutane was employed for the reactions with the (NMTPP)ZnSPr (**2b**)/PrSH and (NMTPP)ZnOMe (**2c**)/MeOH systems, the threo isomers of 3-(propylthio)-2-butanol and 3-methoxy-2-butanol were formed, respectively, as the sole products (runs 1 and 5), while the erythro isomers were exclusively formed when *trans*-2,3-epoxybutane was employed (runs 2 and 6). At an elevated reaction temperature such as 80 °C, the reaction of *trans*-2,3-epoxybutane with the (NMTPP)ZnOMe (**2c**)/MeOH system was considerably accelerated even in the absence of light, but the stereochemical relationship between the substrate and the product was the same as that observed for the reactions under irradiation at 35 °C, and *erythro*-3-methoxy-2-butanol was formed exclusively (run 7). It should be also noted that in the absence of (NMTPP)ZnOMe (**2c**) 2,3-epoxybutanes and MeOH remained unreacted, even at 80

Scheme III



°C under identical conditions (runs 8–10).

The reactions in runs 3 and 4 were carried out without adding PrSH, where 0.5 equiv of 2,3-epoxybutanes was allowed to react with (NMTPP)ZnSPr (**2b**) to suppress the undesired polymerization. The protonolysis of the reaction product between *cis*-2,3-epoxybutane and **2b** ((NMTPP)Zn thiolate) gave *threo*-3-(propylthio)-2-butanol exclusively in 64% yield, as determined by ^{1}H NMR (run 3), while the erythro isomer was obtained in 52% yield when the *trans*-epoxide was reacted under identical conditions (run 4).

Therefore, it can be also concluded clearly that the ring-opening reactions of 2,3-epoxybutanes with the zinc thiolate and alcoholate species of zinc *N*-methylporphyrins (**2**) both take place with inversion of the configuration at the carbon atom of the epoxide ring where cleaved.

Discussion

As already mentioned in the Introduction, anionic ring-opening reactions of epoxides mostly take place with inversion of the configuration (Scheme IA),[1,2] while the reaction involving nondissociative nucleophilic species has a possibility to occur with retention of the configuration (Scheme IB).[3] Polymerizations of epoxides with aluminum porphyrins ((TPP)AlX, **1**) and zinc *N*-methylporphyrins ((NMTPP)ZnX, **2**) exhibit some features which are characteristic of the reaction via nondissociated nucleophilic species. However, contrary to our expectation (Scheme II), the ring-opening reactions of 2,3-epoxybutanes with **1** and **2** both were found to take place with inversion of the configuration. To explain this unexpected stereochemistry of the reactions, we propose linear transition state mechanisms by simultaneous participation of two metalloporphyrin molecules (Scheme III), where one molecule of metalloporphyrin accommodates coordinative activation of epoxide and the other metalloporphyrin molecule serves as a nucleophile to attack the coordinating epoxide from the back side.[27] In this connection, we have already reported that the ring-opening polymerization of a six-membered lactone such as δ-valerolactone via a (porphinato)aluminum alcoholate as the growing species follows the kinetics $\nu_p = k_p[(TPP)AlOR]^2$ [lactone] and proposed a trimolecular mechanism similar to Scheme IIIA, where the monomer is activated by coordination to the opposite side (trans position) of the aluminum porphyrin molecule with respect to the axial group (X).[28] On the contrary, for the reaction with (NMTPP)ZnX (**2**), a mechanism involving the cis coordination of epoxide to **2** is likely (Scheme IIIB), since the opposite side to X of **2** is sterically protected due to the presence of the *N*-methyl group.

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(23) ^{1}H NMR in C_6D_6 (C_6H_6 (δ 7.40) as internal standard): δ −0.80 (t, SCH_2), −0.45 (m, SCH_2CH_2), 0.10 (t, $SCH_2CH_2CH_3$), and −3.83 (s, NCH_3) (see ref 5).

(24) For reference, the alcoholate formed by reaction of **1a** with 1,2-epoxypropane, (TPP)Al–OCH(CH_3)CH_2– (**3**; R′ = CH_3) ($CDCl_3$): δ −1.9 (CH_3) and −2.5 (CH).

(25) For reference (in $CDCl_3$): (meso + racemic)-ClCH(CH_3)CH(CH_3)Cl, δ 60.5 and 61.6; *threo*-PhNHC(O)–OCH(CH_3)CH(CH_3)Cl: δ 58.

(26) For reference, the alcoholate species formed by the reaction of **2b** with 1,2-epoxypropane, (NMTPP)Zn–OCH(CH_3)CH_2– (**4**; R′ = CH_3) (C_6D_6): δ −1.17 (CH_3) and −0.35 (CH).

(27) Attempted kinetic studies on the ring-opening polymerizations of 1,2-epoxypropane with (TPP)AlCl (**1a**) and (NMTPP)ZnSPr (**2b**) or the living polymer (**4**) were unsuccessful. In the case of polymerization using **1a** as the initiator, the kinetic parameters were observed to vary with the initial concentration of **1a**. On the other hand, in the case with **2b** or **4** as the initiator, an induction period was observed.

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