Asymmetric Inducing Effect of Substituents in Chiral Oxazaborolidines on Enantioselective Borane Reduction of Ketones

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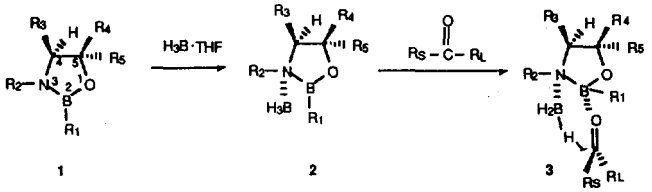
Asymmetric inducing effects of substituents attached at nitrogen, the 5-position and boron in oxazaborolidine rings on asymmetric borane reduction of ketones were investigated. Thus, the effect of N-substituents examined with the oxazaborolidines prepared from (1R, 2S)-N-alkyl norephedrine derivatives showed the remarkable decrease of enantioselectivities of the product alcohols by the variation of the steric size of alkyl groups on nitrogen from Me→*n*-Bu(≃ Bn) →neopentyl→*i*-Pr, such as 83% ee with **5b**, 22% ee with **5c**, 23% ee with **5f**, 16% ee with **5e**, and 3% ee with **5d** for the reduction of acetophenone. The presence of diphenyl groups at the 5-position enhanced the enantioselectivities dramatically. The effect of B-alkyl substituents in the oxazaborolidines derived from (1R, 2S)-ephedrine showed that the enantioselectivities of product alcohols decreased gradually when the substituents were changed from hydrogen to steric bulky groups such as methyl, *n*-butyl, thexyl and phenyl.

Introduction

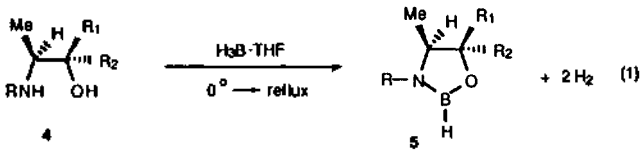
Since Itsuno *et al.* discovered the first effective asymmetric borane reduction of aromatic ketones using chiral 1,3,2-oxazaborolidines prepared *in situ* from the reaction of β-amino-alcohols and borane-tetrahydrofuran complex,[1] a wide variety of chiral oxazaborolidines (**1**) for the asymmetric reduction has been reported.[2] Mechanism of the reduction has been suggested to involve that Lewis acid-base adducts (**2**) formed by reaction of **1** with BH_3-THF serve as effective reagents for the reduction which occur by coordination of the electrophilic boron of the oxazaborolidine on carbonyl oxygen and then intramolecular hydrogen transfer from the >N-BH_3 moiety to the activated carbonyl *via* a six-membered ring



transition state (**3**).[3] The mechanism strongly suggests that the steric and stereoelectronic nature of the substituents attached at nitrogen, boron, and the 4- or 5-positions of the oxazaborolidines would play important roles for their asymmetric inductions. Very recently, we investigated the asymmetric inducing effects of various chiral oxazaborolidines possessing different alkyl groups at the 4-position by comparing the asymmetric borane reduction of the same ketones with each of them.[4] In continuation of our interests on the asymmetric reduction prompted by chiral oxazaborolidines, we undertook to investigate the asymmetric inducing effects of various substituents attached at nitrogen, the 5-position, and boron of chiral oxazaborolidines in the asymmetric borane reductions of ketones.

Results and Discussion

Asymmetric Inducing Effects by Substituents on Nitrogen and the 5-Position of 1. To compare the influence of substituents attached at nitrogen of **1**, we first chose the oxazaborolidines **5a-5f** derived from (1R, 2S)-norephedrine **4a**. The oxazaborolidines were prepared by treatment of the corresponding amino alcohols **4a-4f**[5] with borane-THF in THF at 65 ℃ (Eq. 1). Finally we examined asymmetric induction in the reduction of two representative ketones, such as acetophenone and 2-heptanone, by borane complexed with **5a-f**. The reduction of acetophenone, an aromatic ketone, with each of **5a-c** proceeded readily to be complete within 10 min at room temperature, whereas the reductions with **5d-f** were much slower, requiring a 2 h reaction. The yields were in the range of 89-93%. The effect of N-substituents of **5** on the enantioselection of the product alcohols showed the decrease of enantioselectivity by the variation of the size of R in **5** from Me→*n*-Bu→ neopentyl→*i*-Pr, such as 83% ee with **5b**, 22% ee with **5c**, 16% ee with **5e** and 3% ee with **5d**. The enantioselectivities with **5a** and **5f** were 72% ee and 23% ee, respectively. We also examined the catalytic effects of **5** for the reduction. Thus, the presence of 10 mole % of **5a** and **5b** gave 50% ee and 72% ee, respectively, showing moderate catalytic activities for the asymmetric induction. In contrast, **5c** and **5f** showed low catalytic



a: R = R_2 = H, R_1 = Ph
b: R = Me, R_1 = Ph, R_2 = H
c: R = *n*-Bu, R_1 = Ph, R_2 = H
d: R = *i*-Pr, R_1 = Ph, R_2 = H
e: R = neopentyl, R_1 = Ph, R_2 = H
f: R = Bn, R_1 = Ph, R_2 = H
g: R = R_1 = R_2 = H
h: R = H, R_1 = R_2 = Me
i: R = H, R_1 = R_2 = Ph

effects, providing 5% ee and 9% ee, respectively. In the case of 2-heptanone, an aliphatic ketone, all the reductions with **5** examined were complete within 10 min to give 2-heptanol. Unfortunately, the levels of enantioselection of product alcohols were quite low (0.7-42% ee), although the reaction showed the same trend as in the case of aromatic ketone, *i.e.*,

Table 1. The effect of N-Substituents of Oxazaborolidines for Asymmetric Induction in Enantioselective Borane Reduction of Acetophenone and 2-Heptanone at Room Temperature[a]

Oxazaborolidines	Acetophenone				2-heptanone			
	Time	Yields (%)[b]	% ee[c]	Confg.[d]	Time	Yields (%)[b]	% ee[c]	Confg.[d]
5a	10 min	97	72(50)[e]	R	10 min	96	20	R
5b	10 min	98	83(70)[f]	R	10 min	98	42	R
5c	10 min	98	22(5)	R	10 min	87	8	R
5d	2 h	89	3	R	10 min	96	0.7	R
5e	2 h	91	16	R	10 min	97	8	R
5f	2 h	93	23(9)	R	10 min	93	2	R

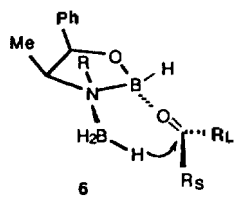
[a]All the reductions were carried out with ketones: **5**: borane-THF (1 : 1 : 1) in THF, unless otherwise indicated. [b]Determined by GC analyses using internal standards. [c]Determined by capillary GC analyses through a Chiraldex GTA chiral column. [d]Determined by comparison of the elution orders of capillary GC analyses through a Chiraldex GTA chiral column and the optical rotations of the corresponding optically active authentic alcohols. [e]The figures in parentheses indicated % ee obtained by the presence of 10 mole % of **5**. [f]Data at 0 ℃ taken in ref. 8.

Table 2. The effect of Substitutents at the 5-Position of Oxazaborolidines for Asymmetric Induction in Enantioselective Borane Reduction of Acetophenone and 2-Heptanone at Room Temperature[a]

Oxazaborolidines	Acetophenone				2-heptanone			
	Time	Yield (%)[b]	% ee[c]	Confg.[d]	Time	Yield (%)[b]	% ee[c]	Confg.[d]
5g	10 min	99	17	R	10 min	98	5	R
5h	10 min	98	25	R	10 min	96	8	R
5i	10 min	98	84	R	10 min	96	54	R

[a-d]See the corresponding footnotes in Table 1.

the decrease of optical purities by increasing the steric bulkness of R in **5**. The results were summarized in Table 1. There are two possible explanations for the results. One is the steric bulkness of alkyl group on nitrogen of **5** which might inhibit an effective coordination of borane to form the oxazaborolidine-borane adducts (**5**-BH_3) which assume to be actual asymmetric reducing species. The free borane may lead the nonasymmetric reduction. This suggestion is in good agreement with the results of the rapid reduction of acetophenone with **5a** and **5b** in contrast to much slower reduction with **5c-i**.[9] The other possible explanation is as follows: when R on nitrogen of **5** is small, the approach of both borane and ketones toward the α face ("endo" **6**) is more favorable to give (R)-alcohols. However, when the R group is sterically bulky, the β facial ("exo" **7**) approach to provide (S)-alcohols may be possible because of steric hindrance between the R group on nitrogen and the methyl group at 4-position in **5**.



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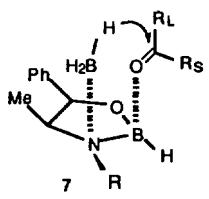

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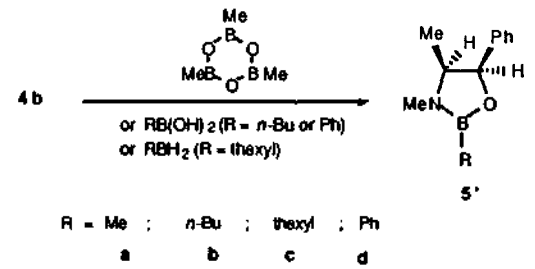
(S)-alcohols

On the other hand, to examine the influence of substituents at the 5-position of **1**, the borane asymmetric reductions of the selected ketones mediated by the oxazaborolidines **5g-5i** were examined. As shown in Table 2, the two representative ketones examined were reduced rapidly to give the corresponding alcohols in high chemical yields. Of the oxazaborolidine examined, **5i** bearing diphenyl groups at the 5-position enhanced remarkably enantioselectivities of the product alcohols, such as 84% ee for acetophenone and 54% ee for 2-heptanone. In contrast, **5g** derived from (S)-alaninol afforded 17% ee for acetophenone and 5% ee for 2-heptanone. **5h** containing dimethyl groups at the 5-position did not show any significant effect for the enhancement of enantioselectivity, providing 25% ee for acetophenone and 8% ee for 2-heptanone.

Asymmetric Inducing Effects by B-Substituents of 1. The B-substituted oxazaborolidines **5'a-d** derived from (1R, 2S)-ephedrine **4b** were chosen as representative. The derivatives were prepared by the reaction of **4b** with the



(2)

Table 3. The effect of Substitutents on Boron of Oxazaborolidines for Asymmetric Induction in Enantioselective Borane Reduction of Acetophenone and 2-Heptanone at Room Temperature[a]

Oxazaborolidines	Acetophenone				2-heptanone			
	Time (h)	Yield (%)[b]	% ee[c]	Confg.[d]	Time (h)	Yield (%)[b]	% ee[c]	Confg.[d]
5'a	1	89	61	R	0.5	92	15	R
5'b	1	90	55	R	0.5	94	13	R
5'c	24	75	48	R	24	78	10	R
5'd	3	85	42	R	1	88	8	R

[a] All the reductions were carried out with ketones: **5'**: borane-THF (1 : 1 : 1) in THF, unless otherwise indicated. [b-d] See the corresponding footnotes in Table 1.

corresponding boroxine, boronic acids and monoalkylborane (Eq. 2), according to the known procedures.[3,5,12] The asymmetric inducing effects by B-substituent groups of **5'** were investigated by comparing enantioselective borane reduction of acetophenone and 2-heptanone in the presence of 1 equiv of **5b** and **5'** in THF at room temperature. As shown in table 3, the reduction of the selected ketones with **5'a-b** and **5'd** were somewhat slower than those with **5b** (R=H in **5'**). The reduction with **5'c** proceeded very sluggishly. For aectophenone, the enantioselectivities induced by B-alkyl (or phenyl) oxazaborolidines **5'** are 61% ee with **5'a**, 55% ee with **5'b**, 48% ee with **5'c** and 42% ee with **5'd**. Compared to 83% ee by **5b** (R=H in **5'**), these selectivities are considerably lower. For 2-heptanone, very low levels of enantioselection were obtained (8-15% ee). The reason for the decrease of reduction rate and enantioselectivities is unclear, but it seems to be attributable to insufficient coordination of carbonyl oxygen to Lewis acidic boron of **5'** due to steric and/or stereoelectronic effects of B-substituted groups.

Conclusion

In the enantioselective borane reduction of ketones induced by chiral oxazaborolidines, the influence of substituents attached at nitrogen, the 5-position and boron of the oxazaborolidine rings was investigated. Thus, substituents of alkyl groups, such as *n*-butyl, benzyl, neopentyl and *iso*-propyl, on nitrogen afforded much lower enantioselectivities of product alcohols as compared to those obtained from substituents of hydrogen or methyl. Alkyl or phenyl substituents on boron decreased the enantioselectivities gradually when the substituents were changed from hydrogen to steric bulky groups, such as methyl, *n*-butyl, thexyl and phenyl. But diphenyl group at the 5-position enhanced the enantioselectivities dramatically. The present study provides the first systematic comparison for asymmetric induction by the variation of substituents at nitrogen, boron and the 5-position in chiral oxazaborolidines on enantioselective borane reduction of ketones.

Experimental

General. All glassware was dried at 140 ℃ overnight, assembled hot, and cooled to room temperature under a stream of nitrogen. All reactions with air sensitive materials were carried out under static pressure of nitrogen. Liquid materials were transferred with double-ended needles.[10]

Spectra. ^{1}H NMR spectra were conducted on Varian Gemini 300 (300 MHz) and Varian T-60 (60 MHz) spectrometers with Me_4Si as an internal standard. IR measurements were recorded on a Shimadzu IR-435 ratio recording spectrophotometer equipped with a Shimadzu data recorder. Optical rotations were measured with a Rudolph polarimeter Autopol III. Melting points were determined with a Fisher-Johns melting point apparatus.

GC analysis. All GC analyses were carried out with Shimadzu GC-7A gas chromatograph and Hewlett-Packard 5890 gas chromatograph equipped with a Hewlett-Packard 3390A integrator/plotter. Optical purities (% ee) were determined by capillary GC analyses of the product alcohols using a Hewlett-Packard 5890 gas chromatograph equipped with a 20 m Chiraldex GTA chiral capillary column.

Materials. Borane-THF, Borane-methyl sulfide (BMS), (1R, 2S)-(−)-norephedrine **4a**, (1R, 2S)-(−)-ephedrine **4b**, (S)-alanine, trimethylboroxine, *n*-butylboronic acid, phenylboronic acid and the other commercially available chemical reagents were purchased from the Aldrich Chemical Co. Thexylborane[11] was prepared by hydroboration of 2,3-dimethyl-2-butene with borane-THF. Tetrahydrofuran was distilled over sodium benzophenone ketyl and stored in ampules under nitrogen pressure. Chiral oxazaborolidines, **5** and **5'** were prepared *in situ* by the literature procedures[3,5,12] and used as themselves for the reduction. N-alkyl norephedrine derivatives **4c-f** and (S)-alaninol derivatives **4g-i** were prepared by the following methods:

Preparation of (1R, 2S)-(−)-N-*n*-butyl norephedrine 4c. According to the literature procedure,[13] THF solution of (1R, 2S)-N-*n*-butyrylnorephedrine[5] (4.42 g, 20 mmol) prepared by reaction of (1R, 2S)-(−)-norephedrine **4a** with *n*-butyryl chloride in methylene chloride in the presence of triethylamine at 0 ℃ was heated to reflux and BMS (3.8 m*l*, 36 mmol) was added in drops over a period of 15 min. Dimethyl sulfide was distilled off and collected in a receiver. After 2 h, the solvent was removed under reduced pressure. To the residue was added *c*-HCl (3.3 m*l*) slowly and the mixture was heated to 100 ℃ for 30 min. After the reaction mixture was cooled down to 0 ℃, 6 N NaOH (5 m*l*) was added. The liberated amine was extracted with ether and the etherial extract was dried over anhydrous potassium carbonate. After the solvent was evaporated *in vacuo*, the product was isolated by distillation: bp. 108-110 ℃/0.15 mmHg; 74% yield; $[\alpha]_D^{22} = -10.97$ (*c* 1.23, $CHCl_3$); ^{1}H NMR (300

MHz, $CDCl_3$) δ 0.81 (3H, d, J=6.5 Hz, CH_3), 0.93 (3H, t, J=7.3 Hz, $CH_3(CH_2)_3N$), 1.33-1.52 (4H, m, $CH_3CH_2CH_2CH_2N$), 2.65-2.75 (2H, m, $-CH_2N$), 2.92 (1H, m, C2-H), 4.75 (1H, d, J=3.9 Hz, C1-H), 7.23-7.34 (5H, m, Ph-H); IR ν (cm^{-1}) 3335, 3022, 2855, 1460, 1128. Using the same procedure, **4e** and **4f** were prepared.

4e: bp. 118-120 ℃/0.2 mmHg; 75% yield; $[\alpha]_D^{22}=-17.42$ (c 1.28 $CHCl_3$); ^1H NMR(300 MHz, $CDCl_3$) δ 0.80 (3H, d, J=6.5 Hz, CH_3), 0.94 (9H, s, $(CH_3)_3CCH_2N$), 2.38 (1H, d, J_{gem}= 12.3 Hz, $-CH_2N$) 2.55 (1H, d, J_{gem}=11.2 Hz, $-CH_2N$), 2.88 (1H, m, C2-H), 4.74 (1H, d, J=3.8 Hz, C1-H), 7.22-7.34 (5H, m, Ph-H); IR ν (cm^{-1}) 3406, 3074, 2942, 1468, 1134.

4f: bp. 158-160 ℃/0.2 mmHg; 70% yield; $[\alpha]_D^{22}=-31.88$ (c 1.01, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 0.88 (3H, d, J=6.0 Hz, CH_3), 2.38 (1H, m, C2-H), 3.90 (2H, s, $-CH_2N$), 4.80 (1H, d, J=4.0 Hz, C1-H), 7.23-7.34 (10H, m, Ph-H); IR ν (cm^{-1}) 3394, 3075, 2966, 1450, 1111.

Preparation of (1R, 2S)-(−)-N-*i*-propyl norephedrine 4d[6]. To a solution of **4a** (6.1 g, 40 mmol) and sodium cyanoborohydride (1.8 g, 28.6 mmol) in methanol (60 m*l*) was added acetone (3.3 m*l*) at room temperature. After the reaction mixture was stirred for 18 h under nitrogen pressure, evaporation of solvent provided **4d** as a white solid: mp. 123-125 ℃; 68% yield; $[\alpha]_D^{22}=-9.1$ (c 1.01, 1 N HCl); ^1H NMR (300 MHz, $CDCl_3$) δ 0.82 (3H, d, J=6.0 Hz, CH_3), 1.12 (6H, d, J=7.0 Hz, $(CH_3)_2CHN$), 2.15 (1H, d, C2-H) 2.93-3.23 (1H, m, $(CH_3)_2CHN$), 4.73 (1H, d, J=4.0 Hz, C1-H), 7.23-7.34 (5H, m, Ph-H); IR ν (cm^{-1}) 3344, 3057, 2918, 1585, 1469, 1146.

Preparation of (S)-alaninol 4g. According to the literature,[14] **4g** was obtained from reduction of (S)-alanine.

Preparation of (S)-2-amino-1,1-diphenylpropane-1-ol 4i[15]. **4i** was obtained in 67% yield from (S)-alanine methyl ester hydrochloride[16] (4.18 g, 30 mmol) and phenylmagnesium bromide (240 mmol) in ether by the known method[15]: mp. 104 ℃ [lit.[15] 100-102 ℃]; ^1H NMR (60 MHz, $CDCl_3$) δ 0.87 (3H, d, J=6.0 Hz, CH_3), 1.60-2.37 (1H, m, C2-H), 7.02-7.80 (10H, m, Ph-H); IR ν (cm^{-1}) 3422, 3074, 2927, 1446, 1173, 704. With the same method, **4h** was prepared from (S)-alanine methyl ester hydrochloride[16] and methylmagnesium bromide in ether.

4h: oil; ^1H NMR (60 MHz, $CDCl_3$) δ 0.87 (3H, d, J=6.0 Hz, CH_3), 1.04 (3H, s, CH_3), 1.22 (3H, s, CH_3), 1.60-2.37 (1H, m, C2-H); IR ν (cm^{-1}) 3415, 2958, 1260, 1107.

Asymmetric Borane Reduction of Ketones in the presence of N-alkyl oxazaborolidines 5a-f. The reduction of acetophenone with **5a** is representative. Into the flask equipped with a side arm, a magnetic stirring bar, and a reflux condenser was added **4a** (207 mg, 1 mmol) in anhydrous THF (2 m*l*). To this was added borane-THF (1 mmol, 1 m*l*) slowly in an ice bath. After hydrogen evolution was ceased, the reaction mixture was heated to reflux for 2 h. The volatiles were then pumped off to furnish a white solid of **5a**. Under nitrogen atmosphere, **5a** was dissolved in anhydrous THF (1 m*l*), followed by addition of borane-THF (1 mmol, 1 m*l*) at 0 ℃. The mixture was stirring for 1 h at 0 ℃. To this was added a solution of acetophenone (120 mg, 1 mmol) in THF (0.5 m*l*) at room temperature (*ca.* 25 ℃). The reaction mixture was stirred for 10 min at the same temperature and then excess hydride was decomposed by addition of 1 N HCl. After solvent was removed *in vacuo*, the residue was extract with ethyl ether. The ether layer was washed with saturated NaCl solution and dired over anhydrous magnesium sulfate. GC analysis indicated the formation of 1-phenylethanol in 97% yield. After evaporation of solvent, the product was isolated by bulb-to-bulb distillation. The enantioselectivity of product alcohol determined by capillary GC analysis through a 20 m Chiraldex GTA chiral column was 72% ee, R.

The data of reduction using other N-alkyl oxazaborolidines were summarized in Table 1.

Asymmetric Borane Reduction of Ketones in the Presence of Oxazaborolidines 5g-i. The reduction of acetophenone with **5i** is representative. **5i** was obtained from **4i** and borane-THF with the same procedure as described above. The reduction and work-up procedures were adopted with the same conditions as those mentioned above. GC analysis showed the presence of 1-phenylethanol in 98% yield. The optical purity of product alcohol determined was 84% ee, R.

The data of reduction using other oxazaborolidines **5g-h** were summarized in Table 2.

Asymmetric Borane Reduction of Ketones in the Presence of B-substituted Oxazaborolidines 5'a-d. The reduction of acetophenone with **5'a**[17] is representative. To a hot (80 ℃) solution of **4b** (500 mg, 3 mmol) in toluene (20 m*l*) was added trimethylboroxine (250 mg, 1.98 mmol) all at once and heating bath was removed. After the reaction mixture was stirred for 18 h at room temperature, solvent was distilled off at atmospheric pressure. To ensure the removal of methanol produced, dry toluene (10 m*l*) was added to the residue and distilled off. Finally, the solvent was removed completely *in vacuo* and the residue **5'a** was diluted with dry THF to become 1 M solution. The reduction and work-up procedures were adopted with the same conditions as those mentioned above. GC analysis showed the presence of 1-phenylethanol in 89% yield. The optical purity of product alcohol determined was 61% ee, R.

The data of reduction using other oxazaborolidines **5'b-d** were summarized in Table 3.

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ropylnorephedrine **4d** were obtained in a 68% yield by reductive alkylation of **4a** with acetone and sodium cyanoborohydride[7]: for detailed procedure and physical properties of the products **4c-f**, see experimental section.
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Study on Equivalent Circuits of Sodalite Type Materials by Complex Impedance Analysis

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Electrical characteristics of Fe-substituted sodalites were analyzed and equivalent circuits of samples were designed using impedance and admittance data. Internal components of resistances (R_i, R_b, and R_{gb}) and capacitances (C_b, C_{gb} and C_D) could be extracted by changing the frequency of measurement at three different temperatures. Upon increasing the temperature, electrical properties of the samples could be elucidated in detail by equivalent circuit. The substitution of Fe on Al site was indirectly confirmed by ESCA and the results explain the lower polarity in Na-O bond of Fe 10 mole %-substituted sodalite.

Introduction

Isomorphous substitution of Al by Fe up to 25 mole % in sodalite framework has been carried out and its ionic semiconducting property has been studied.[1] For a conductivity measurement of polycrystalline materials, it is well known that AC method has many advantages because interfacial polarization between the blocking electrode-material (electrolyte) and grain boundary effects can be sorted out at proper frequencies. This method has been used by many scientists, especially for various solid electrolytes.[2-9]

The complex method originates from Cole and Cole complex permittivity diagrams.[10] The complex admittance (Y) can be expressed as the sum of the conductance (G) and the susceptance (B).

$$Y = G + iB$$

Again, the complex impedance (Z) which is reciprocal of complex admittance (Y^{-1}) separates into real and imaginary components, *i.e.*

$$Z = R + jX$$

Where R is resistance and X is reactance. From the plot of B *vs.* G (Scheme 1), the resistance value can be derived from the circular arc intercept on the G-axis, and the capacitance value from the expression involving the frequency at the peak of the circular arc. When the admittance plot gives a circular arc, a series R-C circuit is dominant, whereas a straight line indicates more characteristic parallel R-C circuit as can be seen in Scheme 1.

Here we report new results on polycrystalline solids in extension of our previous work.[1] And we designed equivalent circuits of Fe-substituted sodalites by analysing the electrical data; the contribution of electronic resistance, resistances of grain and grain boundary, bulk capacitance, capacitance of electrode-material (electrolyte) interface, and dipole capacitance. These interpretations will facilitate the understanding of electrical characteristics and applications. ESCA analysis was also carried out to obtain relative compositions of samples and compare the bond polarity. Results were discussed in