

Synthesis of new C_2 -symmetric bioxazoles and application as chiral ligands in asymmetric hydrosilylation

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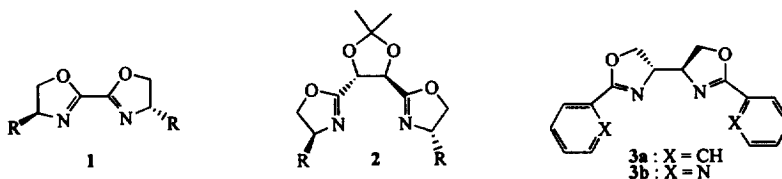
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Abstract: New C_2 -symmetric chiral (4*S*,4'*S*)-bioxazoles **3a** and **3b**, possessing chirality on their backbone, were synthesized efficiently starting from L-tartaric acid. The structure of **3a** was determined by X-ray crystal structure analysis. With these novel chiral bioxazole ligands, as a preliminary investigation for their effects on the enantioselectivity, rhodium(I)-catalyzed enantioselective hydrosilylations of acetophenone were carried out. © 1997 Published by Elsevier Science Ltd

Introduction

In 1989, there were several reports for the use of enantiomerically pure oxazolines as ligands in catalytic asymmetric hydrosilylation.¹ Since then, much effort has been directed to the design and synthesis of new kinds of chiral oxazoline ligands for metal mediated catalysis.² Recently, to reduce the number of stereochemical permutations within the catalytic ensemble, a series of C_2 -symmetric methylene bisoxazoles, in which the two oxazolines are separated by a methylene backbone, were used in various catalytic processes, and thereby afford high levels of enantiocontrol.³

However, only a few C_2 -symmetric bioxazoles **1**, where the two oxazoline rings are bonded directly, have been reported and their catalytic activities in Cu, Ir, Pd, Rh catalysed asymmetric reactions (cyclopropanation,^{3f} hydrogen transfer reaction,^{3c} allylic alkylation^{3c} and hydrosilylation^{3d}) examined. Moreover, although the bisoxazoles **2** have been reported,^{3l,m} none of the reported C_2 -symmetric bioxazoles and methylene bisoxazoles possess chirality on their backbone.



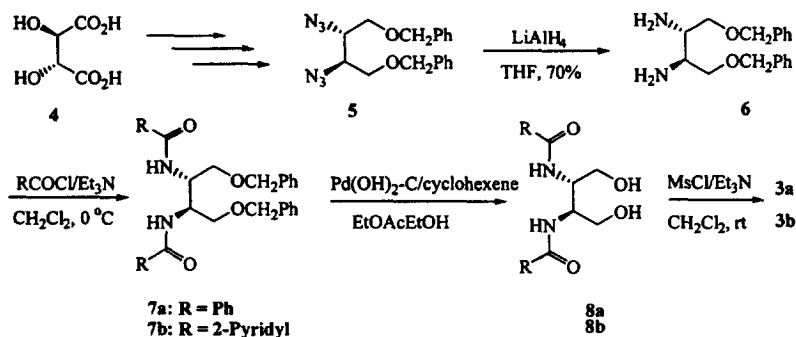
Therefore, we became concerned with the preparation of ligands which possess stereogenic centers on their backbone. In this article we report the preparation and application as chiral ligands in asymmetric hydrosilylation to the new C_2 -symmetric (4*S*,4'*S*)-bioxazoles **3**.

Results and discussion

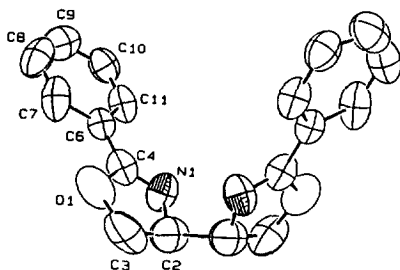
For the synthesis of the C_2 -symmetric (4*S*,4'*S*)-bioxazoles **3a** and **3b**, optically active vicinal diamine **6** could be an important building block which was easily and efficiently synthesized starting from L-tartaric acid as shown in Scheme 1.

Diazide **5** was prepared from (2*R*,3*R*)-(+)-tartaric acid **4** according to previously reported procedure^{4,5} in a six-step synthesis (60% overall yield), then transformed into diamine **6** by reduction with $LiAlH_4$ in 70% yield. Very recently, during preparation of this manuscript, Mosset *et al.* published

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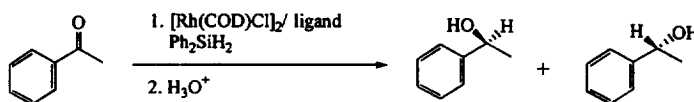
Scheme 1.

Figure 1. ORTEP drawing of compound **3a**.

that the diamine **6** can be obtained by selective azide reduction of **5** using Pd–C/H₂ in quantitative yield.⁶ The crude diamine **6** was easily converted into its benzamide **7a** by reaction with benzoyl chloride in 81% yield, after chromatographic purification on silica gel. Debencylation of **7a** using Pd–C under an atmospheric pressure of H₂, even at higher pressure (30 psi using Par hydrogenation reactor), was not efficiently accomplished (after 48 h, about 50% conversion was achieved along with the monodebenzylated product). However, when the dibenzyl ether **7a** was refluxed in the presence of Pd(OH)₂–C/cyclohexene in ethyl acetate–methanol (1:1, v/v) for 24 h, the debenzylated diol **8a** was obtained in quantitative yield. For the synthesis of the desired C₂-symmetric bioxazole **3a**, initially, the diol **8a** was converted to the corresponding dichloride by reaction with thionyl chloride, then, the resulting dichloride was treated with NaOH to give only 20% overall yield (from **8a**) of the desired (4*S*,4'*S*)-bioxazole **3a**. However, the yield of **3a** was increased to 59% by reaction of the diol **8a** with methanesulfonyl chloride in the presence of triethylamine according to the procedure reported by Denmark.⁷ The ring closure occurred simultaneously during mesylation. An enantiomerically pure, single crystal of **3a** suitable for X-ray crystallography was obtained by recrystallization with diethyl ether. An unambiguous structure of **3a** (Figure 1) was determined by spectroscopic and X-ray analysis. The bis(pyridyl)-bioxazole **3b** was also synthesized from **7b** in a similar manner to **3a** in 47% overall yield from **6**.

Having the new kind of bioxazole ligands in hand, as a preliminary investigation of their effects on the enantioselectivity, rhodium(I)-catalyzed enantioselective hydrosilylations of acetophenone were carried out without solvent. Thus, hydrosilylation of acetophenone with diphenylsilane using ligand **3a** without solvent afforded 1-phenylethanol in 44% ee. When the same reaction was carried out using ligand **3b**, the enantioselectivity was increased slightly to 50% ee. The enantioselectivities were not very high, however, it should be noted here that the reaction conditions were not optimized, nevertheless, the observed enantioselectivities are comparable with those of the reported bioxazoles **1**^{3d} and bisoxazoles **2**.^{3m} For example, hydrosilylation of acetophenone using bioxazole **1** exhibited

0–84% ee^{3d} and 12–65% ee using bisoxazole 2.^{3m} Moreover, ligand **3** gave higher enantiomeric discrimination than that with the ligand **2** (R=H, 12% ee in CCl₄ solvent). One of the reasons for the higher selectivity of ligand **3** may be due to formation of five-membered ring chelate with metal ions than the ligand **2**, for which a seven-membered ring chelate is expected.



ligand	time (h)	temp (°C)	conversion(%) ^a	% ee ^b	config. ^c
3a	30h	8	54.4	44	<i>R</i>
3b	30h	8	75.5	50	<i>R</i>

Condition: ligand (0.34 mmol), [Rh(COD)Cl]₂ (0.04 mmol), PhCOCH₃ (6 mmol), Ph₂SiH₂ (6.6 mmol), no solvent. ^a Determined by methyl signals of ketone (δ 2.55) and alcohol (δ 1.43) in ¹H NMR spectrum of the crude product. ^b Determined by ¹H NMR (CDCl₃) of its (*S*)-MTPA ester.

^c Determined by major (CH₃O) signal of its (*S*)-MTPA ester in ¹H NMR (CDCl₃) spectrum: δ 3.55 for (*R*)-enantiomer and 3.46 for (*S*)-enantiomer. ^d

Conclusion

In summary, the new C₂-symmetric enantiomerically pure (4*S*,4'*S*)-bioxazoles **3a** and **3b** were efficiently synthesized starting from L-tartaric acid. These are the first C₂-symmetric bioxazoles possessing chirality on their backbone. With these compounds as chiral ligands, the rhodium-catalyzed asymmetric hydrosilylations of acetophenone were carried out, and it was found that chirality of the backbone in ligand **3** has a significant effect on the enantiomeric discrimination. Further studies on the design, synthesis and the potential of this kind of ligand for metal-catalyzed asymmetric reactions are in progress.

Experimental

General

¹H NMR and ¹³C NMR were recorded on a Varian Gemini 300 MHz spectrometer with TMS as internal reference, IR spectra were recorded on a MIDAC 101025 FT-IR spectrometer and optical rotation was measured with Autopol[®] polarimeter. Chemical analyses were carried out by the Advanced Analysis Center at KIST. Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Column chromatography was performed on Kieselgel 60 (230–400 mesh) and TLC was carried out using glass sheets precoated with silica gel 60F254 purchased from Merck.

(2*S*,3*S*)-1,4-Bis(benzyloxy)-2,3-diaminobutane **6**

Diazide **5** was prepared from L-(+)-tartaric acid according to lit.^{4,5} in a six step synthesis (60% overall yield). To a suspension of LiAlH₄ (17 g, 447.9 mmol) in THF (300 mL) was added dropwise a THF (50 mL) solution of diazide **5** (19.18 g, 54.43 mmol) at 0°C. The reaction mixture was refluxed for 24 h, then quenched with saturated Na₂SO₄ aqueous solution at 0°C. The white solid which appeared was filtered off and the filter cake was washed with hot THF (3×100 mL). The combined filtrate was dried over anhydrous MgSO₄ and evaporated under reduced pressure to give colorless viscous liquid which crystallized after storage for one day in a freezer yielding 11.4 g (70%) of white solid **6** which was used for next reactions without further purification. m.p. 45–47°C (46–47°C in lit.⁶); ¹H NMR (300 MHz, CDCl₃) δ 7.34–7.25 (m, 10H), 4.51 (s, 4H), 3.48 (dd, *J*=9.2, 4.4 Hz, 2H), 3.41 (dd, *J*=9.2, 6.4 Hz, 2H), 3.02 (m, 2H), 1.41 (bs, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 138.37, 128.45, 128.32, 127.70, 127.55, 73.67, 73.28, 52.79, 52.60.

(2S,3S)-1,4-Bis(benzyloxy)-2,3-[N,N'-bis(benzoyl)]diaminobutane 7a

Benzoyl chloride (4.8 mL, 40.95 mmol) was added to a solution of diamine **6** (4.1 g, 13.6 mmol) and triethylamine (7.6 mL, 54.59 mmol) in anhydrous methylene chloride (60 mL) at 0°C. After stirring for 2 h at 0°C, the reaction mixture was quenched by addition of water. Organic layer was separated and the aqueous layer was extracted with methylene chloride (3×20 mL). Combined organic phases were successively washed with saturated NaCl aqueous solution and water, dried (MgSO₄) and concentrated. The resulting yellowish solid was purified by recrystallization with ether to give **7a** (5.6 g, 81%) as a white solid. $R_f=0.45$ (ethyl acetate:*n*-hexane=2:1); $[\alpha]_D^{24}=-76.9$ (c 1.0, CHCl₃); m.p. 113–114°C; ¹H NMR (300 MHz, CDCl₃) δ 7.65 (d, $J=8.4$ Hz, 4H), 7.45 (m, 2H), 7.36–7.26 (m, 14H), 4.69 (m, 2H), 4.51 (bs, 4H), 3.75 (dd, $J=9.8, 3.2$ Hz, 2H), 3.69 (dd, $J=9.8, 4.5$ Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 16.76, 137.44, 133.89, 131.39, 128.47, 128.41, 127.98, 126.92, 73.50, 68.90, 50.96; IR (KBr) ν 3316, 3062, 2866, 1636, 1538, 1348, 1110 cm⁻¹; Anal. Calcd for C₃₂H₃₂N₂O₄: C,75.57; H,6.34; N,5.51. Found: C,75.5; H,6.36; N,5.58.

(2S,3S)-1,4-Bis(benzyloxy)-2,3-[N,N'-bis(picolinyl)]diaminobutane 7b

To a suspension of picolinic acid (2.58 g, 20.97 mmol) in anhydrous methylene chloride (30 mL) was added oxalyl chloride (3.55 g, 27.96 mmol) and 2 drops of DMF at 0°C. The reaction mixture was stirred for 5 h at room temperature, and then excess oxalyl chloride and solvent were removed under reduced pressure. The residue was suspended in anhydrous methylene chloride (40 mL) and the reaction temperature was allowed to cool to 0°C. A solution of diamine **6** (2.1 g, 6.99 mmol) in anhydrous methylene chloride (10 mL) and triethylamine (10 mL, 66.4 mmol) were successively added. After further stirring for 4 h at the same temperature, the reaction was quenched by addition of water. The organic phase was washed successively with saturated NaHCO₃ aqueous solution and water and brine, and dried (MgSO₄) and concentrated using rotavap. The residue was purified by column chromatography on silica gel to give **7b** (2.93 g, 82%) as a white solid: $R_f=0.65$ (ethyl acetate:*n*-hexane=2:1); $[\alpha]_D^{24}=-62.5$ (c 1.0, CHCl₃); m.p. 97–98°C; ¹H NMR (300 MHz, CDCl₃) δ 8.73 (d, $J=8.2$ Hz, 2H), 8.47 (d, $J=4.2$ Hz, 2H), 8.10 (d, $J=7.8$ Hz, 2H), 7.76 (t, $J=7.6$ Hz, 2H), 7.37–7.23 (m, 12H), 4.73 (m, 2H), 4.53 (m, 4H), 3.72 (m, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 164.43, 149.68, 148.13, 137.80, 137.00, 128.29, 127.77, 127.59, 125.94, 122.12, 73.33, 69.38, 50.20; IR (KBr) ν 3356, 1666, 1590, 1570, 1518, 1466, 1434, 1372, 1292, 1092, 998, 746, 694 cm⁻¹; Anal. Calcd for C₃₀H₃₀N₄O₄: C,70.57; H,5.92; N,10.97. Found: C,70.5; H,5.95; N,10.87.

(2S,3S)-2,3-[N,N'-Bis(benzoyl)]diamino-1,4-butanediol 8a

To a solution of dibenzyl ether **7a** (3.81 g, 7.49 mmol) in dry methanol (30 mL) and ethyl acetate (30 mL) were added 10% Pd(OH)₂/C (300 mg) and cyclohexene (10 mL). The reaction mixture was refluxed for 24 h. The catalyst was removed by filtration over celite and the filtrate was concentrated under reduced pressure to remove volatile materials to give crude white solid which was purified by recrystallization with methylene chloride/diethyl ether to give pure diol **8a** (2.38 g, 97%) as a white solid: $R_f=0.2$ (ethyl acetate:*n*-hexane=2:1); $[\alpha]_D^{24}=-5.47$ (c 1.0, CH₃OH); m.p. 174–175°C; ¹H NMR (300 MHz, DMSO-*d*₆) δ 8.31 (d, $J=7.9$ Hz, 2H), 7.85 (d, $J=8.2$ Hz, 4H), 7.52–7.42 (m, 6H), 4.89 (bs, 2H), 4.37–4.32 (m, 2H), 3.56 (d, $J=5.3$ Hz, 4H); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 171.15, 138.57, 135.03, 132.05, 131.28, 64.62, 56.06; IR (KBr) ν 3329, 1634, 1532, 1348, 1068, 1032, 964 cm⁻¹; Anal. Calcd for C₁₈H₂₀N₂O₄: C,65.84; H,6.14; N,8.53. Found: C,65.8; H,6.14; N,8.50.

(2S,3S)-2,3-[N,N'-Bis(picolinyl)]diamino-1,4-butanediol 8b

Prepared from **7b** in a similar manner to **8a**, 98% yield. White solid; $R_f=0.1$ (ethyl acetate:*n*-hexane:methanol=4:1:0.1); $[\alpha]_D^{24}=-94.3$ (c 1.0, EtOH); m.p. 144–145°C; ¹H NMR (300 MHz, CDCl₃) δ 8.52 (d, $J=4.3$ Hz, 2H), 8.26 (d, $J=8.6$ Hz, 2H), 8.19 (d, $J=7.7$ Hz, 2H), 7.86 (t, $J=7.7$ Hz, 2H), 7.46–7.42 (m, 2H), 4.55–4.51 (m, 2H), 4.36 (t, $J=7.0$ Hz, 2H), 3.91–3.85 (m, 2H), 3.73–3.67 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 165.86, 148.02, 148.23, 137.42, 126.59, 122.48, 61.96, 51.57;

IR (KBr) ν 3358, 1672, 1516, 1468, 1436, 1044, 998, 752, 620 cm⁻¹; Anal. Calcd for C₁₆H₁₈N₄O₄: C,58.17; H,5.49; N,16.96. Found: C, 57.9; H, 5.45; N,16.28.

(4S,4'S)-2,2'-Diphenyl-4,4',5,5'-tetrahydro-4,4'-bi(1,3-oxazole) 3a

To a solution of diol **8a** (0.47 g, 1.43 mmol) and triethylamine (2 mL, 25.2 mmol) in anhydrous methylene chloride (20 mL) was added methanesulfonyl chloride (0.34 mL, 4.3 mmol) at 0°C, and then the reaction mixture was stirred for 24 h at room temperature. The reaction was quenched by addition of water at 0°C and extracted with methylene chloride. The organic layer was successively washed with 2% HCl solution and brine, and dried over anhydrous Na₂SO₄, filtered, evaporated. The residue was purified by crystallization with diethyl ether to give **3a** 0.25 g (59%) as a white solid: R_f=0.5 (ethyl acetate:*n*-hexane=2:1); [α]_D²⁴-23.5 (c 0.54, CHCl₃); m.p. 135–137°C; ¹H NMR (300 MHz, CDCl₃) δ 7.92 (d, *J*=6.8 Hz, 4H), 7.48–7.37 (m, 6H), 4.85 (m, 2H), 4.31 (dd, *J*=9.0, 9.2 Hz, 2H), 4.30 (dd, *J*=8.0, 9.2 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 165.70, 131.86, 128.66, 127.72, 69.25, 69.09; IR (KBr) ν 2906, 1650, 1494, 1364, 1320, 1084, 1068, 1022, 936, 784, 696 cm⁻¹.

Crystal data for 3a

The X-ray data were collected on an Enraf-Nonius CAD-4 automatic diffractometer with graphite-monochromated Mo K α (λ =0.71073 Å) at ambient temperature. The structure was solved by the Patterson method (SHELXS-86) and were refined by full-matrix least-square technique. C₁₈H₁₆N₂O₂, M=292.33. Monoclinic-C, a=10.8650(12), b=6.536(3), c=11.3996(13) Å, α =90.00(2)°, β =108.20(9)°, λ =90.00(2)°, Space group=C2 (No. 5), V=767.8(4) Å³, Z=2, D_c=1.264 g/cm³, Crystal size=0.1×0.3×0.5 mm, F(000)=308, a total of 583 reflections in the range of 1.88°≤ θ ≤24.96° measured, the $\Delta\rho_{\max}$ and $\Delta\rho_{\min}$ are 0.380 and -0.405 e Å⁻³, Goodness-of-fit=1.042, 548 independent reflections with I/ σ (I)≥2.0, R=0.11.

(4S,4'S)-2,2'-Di(2-pyridyl)-4,4',5,5'-tetrahydro-4,4'-bi(1,3-oxazole) 3b

Prepared from **8b** in a similar manner to **3a**, 58% yield as a white solid: R_f=0.4 (ethyl acetate:methanol=5:1); [α]_D²⁴-58.1 (c 1.0, CHCl₃); m.p. 128–130°C; ¹H NMR (300 MHz, CDCl₃) δ 8.72 (d, *J*=4.4 Hz, 2H), 8.02 (d, *J*=7.7 Hz, 2H), 7.76 (pseudo t, *J*=7.7 Hz, 2H), 7.39 (dd, *J*=7.7, 4.4 Hz, 2H), 4.95 (m, 2H), 4.56 (pseudo t, *J*=9.6 Hz, 2H), 4.46 (pseudo t, *J*=9.4 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 166.06, 149.02, 148.43, 137.63, 126.79, 122.68, 62.16, 51.77; IR (KBr) ν 3422, 3050, 2906, 1652, 1576, 1470, 1374, 1324, 1264, 1120, 1102, 1086, 1036, 936, 806, 752, 692 cm⁻¹; Anal. Calcd for C₁₆H₁₄N₄O₂: C,65.30; H,4.79; N,19.04. Found: C,65.3; H,4.74; N,19.21.

General procedure for hydrosilylation of acetophenone

The catalyst was prepared *in situ* by dissolving [Rh(cod)Cl]₂ (10 mg, 0.04 mmol) and ligand **3a** or **3b** (0.34 mmol) in the acetophenone (0.7 mL, 6 mmol), then degassed and stirred for 1 h. Diphenylsilane (1.2 mL, 6.6 mmol) was added to the mixture at 8°C and further stirred at same temperature for 30 h. For workup, to the reaction mixture was successively added methanol (5 mL) and 0.1 N HCl solution (10 mL) at 0°C, and the solution was stirred at same temperature for 1 h. The mixture was neutralized by adding 5 mL of saturated aqueous Na₂CO₃ solution and extracted with diethyl ether. The organic layer was dried over anhydrous Na₂SO₄, filtered, concentrated. The conversion yields were determined by comparison of the methyl signals at 2.55(s) and 1.43 (d, *J*=6.5 Hz) in ¹H NMR (300 MHz, CDCl₃) spectrum of the crude product. For measuring enantiomeric excess, product was purified by silica gel column, and then converted to the corresponding MTPA ester with (*S*)-(-)-MTPA and SOCl₂ to give (CH₃O) δ 3.55 for (*R*)- and 3.46 for (*S*)-enantiomer in ¹H NMR (300 MHz, CDCl₃) spectrum.⁸

Acknowledgements

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