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ORIGINAL ARTICLE

Synthesis Of Schiff's Base Ligands By Condensation Of 2-hydroxyacetophenone And Chiral Diamines

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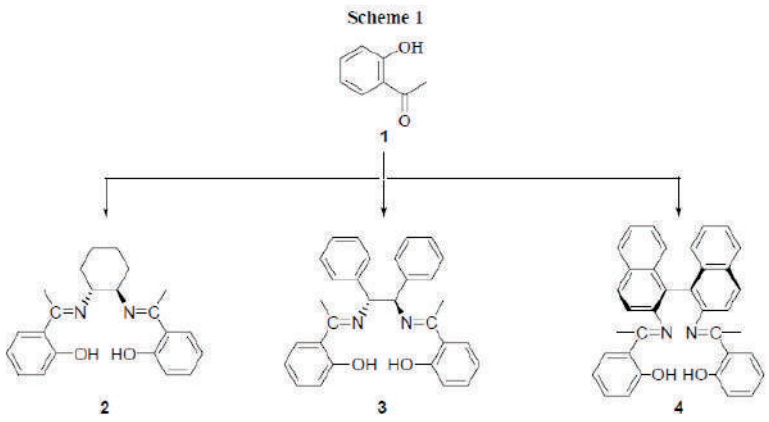
Abstract:

Three optically active Schiff-base ligands 2-4 have been prepared by thermal condensation of 2-hydroxyacetophenone 1 with (1R,2R)-(-)-1,2-diaminocyclohexane, (1S,2S)-(-)- 1,2-diphenylethylenediamine or R-(+)-2,2'-diamino-1,1'-binaphthalene, respectively. The products have been characterized by their elemental analysis, IR, 1H-NMR spectra.

KEYWORDS:

Schiff-base, 2-hydroxyacetophenone, chiral diamines

Scheme 1



INTRODUCTION

Schiff-base ligands derived from salicylaldehyde and chiral amines have been widely applied in enantioselective cyclopropanation of styrenes [1], asymmetric aziridination of olefins [2], enantioselective epoxidation [2,3], enantioselective ring opening of epoxides [3,4], borohydride reduction of aromatic ketones [4], asymmetric oxidation of methyl phenyl sulfide [5], enantioselective oxidation of silyl enol [6] and trimethylsilylcyanation of benzaldehydes [4,7]. In particular the Merck company has successfully

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developed a process for the industrial manufacture of antibacterial drug Cilastatin using chiral copper (II) Schiff-base complexes derived from salicylaldehyde and chiral amine [8]. However, so far there have been few reports about the synthesis and application of Schiff-base ligands derived from 2-hydroxyacetophenone and chiral amines. In order to investigate the electronic, steric and geometric effect of a methyl group on an imine carbon on asymmetric catalytic reactions, 2-hydroxyacetophenone (1) was chosen to synthesize Schiff-base ligands 2, 3, 4 by the condensation with chiral diamines such as 1,2-diaminocyclohexane, 1,2-diphenylethylenediamine and 2,2'-diamino-1,1'-binaphthalene (Scheme 1).

EXPERIMENTAL

General

Reactions were carried out under dry argon or in vacuo. All solvents were dried and degassed prior to use. Infrared spectra were recorded on a Perkin-Elmer spectrophotometer (Model-577) in KBr discs and CH2Cl2. All the melting points were determined in an open capillary and are uncorrected. All glassware was oven dried at 120oC, molecular weight of the complexes was determined cryoscopically in benzene. NMR spectra were recorded on a BRUKER BRX 400 spectrometer and chemical shifts are expressed in ppm using TMS as internal standard. Elemental analysis was performed on a PE-2400 elemental analyzer.

Synthesis of N,N'-(1R,2R)-(-)-1,2-cyclohexylenebis(2-hydroxyacetophenonylideneimine) (2).

To a solution of (1R,2R)-(-)-1,2-diaminocyclohexane(140mg, 1.23mmol) in absolute ethanol (1mL) was added 2-hydroxyacetophenone 1 (334mg, 2.46mmol). The resulting mixture was then refluxed for 36 h. After cooling to room temperature, water (5mL) was added and the mixture stirred for 30 min, the yellow precipitate formed was filtered, washed with water and dried. Recrystallization from absolute ethanol afforded yellow needles (303mg, 70.5%); mp: 144-145ºC;[]D^{24}= -788.12° (c =1.1×10^{3} in CH_2Cl_2); IR (neat) cm^{-1}: 3060 (OH), 1618 (C=N);^{1}H-NMR($CDCl_3$):16.40 (s, 2H, OH), 7.37-6.67 (m, 8H, Ar-H), 3.86 (d, 2H, CH), 3.05 (s, 6H, CH_3), 1.92-1.46 (m, 8H,CH_2CH_2); Anal.: Calcd. for $C_{22}H_{26}N_2O_2$:C, 75.40; H, 7.48; N, 7.99; Found: C, 75.25; H, 7.26; N, 7.85.

Synthesis of (1S,2S)-(-)- 1,2-diphenylethylenebis(2-hydroxyacetophenonylideneimine) (3).

To a solution of (1S,2S)-(-)-1,2-diphenylethylenediamine (212mg, 1.00mmol) in absolute toluene (3mL) was added 2-hydroxyacetophenone 1 (272mg, 2.00mmol) and activated alkaline aluminum oxide (100mg, 0.98mmol). The resulting mixture was refluxed with stirring for 24 h. After the aluminum oxide was filtered off, the solvent was evaporated in vacuo to gave a yellow solid.

Chromatography on silica (elution with 10% EtOAc/petroleum ether) afforded bright yellow crystals

(312mg, 69.6%), mp: 173-175ºC; []D^{19}= -138.03°(c=1 in $CHCl_3$); IR (neat) cm_{-1}: 3062 (OH), 1618(C=N); ^{1}H-NMR($CDCl_3$): 16.06 (s, 2H, OH), 7.39-6.68 (m, 18H, Ar-H); 5.26 (s, 2H, CH),2.26 (s, 6H, CH_3); Anal.: Calcd. for $C_{30}H_{28}N_2O_2$:C, 80.33; H, 6.29; N, 6.25; Found: C, 80.12; H, 6.26; N, 6.10.

Synthesis of R-(+)-1,1'-binaphthalene-2,2'-diaminobis(2-hydroxyacetophenonylideneimine) (4).

To a solution of R-(+)-2,2'-diamino-1,1'-binaphthalene (284mg, 1.00mmol) in absolute toluene (3mL) was added 2-hydroxyacetophenone 1 (272mg, 2.00mmol) and activated alkaline aluminum oxide (125mg, 1.23mmol). The resulting mixture was refluxed with stirring for 72 h. After the aluminum oxide was filtered off, the solvent was evaporated in vacuo to gave a yellow solid.

Chromatography on silica (10% EtOAc/petroleum ether) afforded bright yellow needles (118mg,25.1%), mp: 262-264º; []D18= 15.87°(c=0.232 in CHCl); IR (neat) cm-1: 3065 (OH), 1618 (C=N);1H-NMR ($CDCl_3$): 15.58 (s, 2H, OH), 7.89-6.67 (m, 20H, Ar-H), 2.17 (s, 6H, CH_3); Anal.: Calcd. for $C_{36}H_{28}N_2O_2$:C, 83.05; H, 5.42; N, 5.38; Found: C, 83.01; H, 5.11; N, 5.13.

RESULTS AND DISCUSSION

The Schiff-base ligand 2 was easily prepared in 70.5% yield by refluxing two equivalents of 2-hydroxyacetophenone (1) with (1R,2R)-(-)-1,2-diaminocyclohexane in anhydrous ethanol.Complete condensation of all primary amino groups is confirmed by the lack of N-H stretching bands in the 3150-3450cm-1 IR region and the presence of strong C=N stretching bonds. The 1H-NMR and infrared data for 2 are completely consistent with the formulation indicated in Scheme 1. After we failed to synthesize the Schiff-base ligands of 2-hydroxyacetophenone and chiral 1,2-diphenylethylenediamine and 2,2'-diamino-1,1'-binaphthalene using the method described above, we tried replacing the solvent anhydrous ethanol with butanol to increase the reaction temperature and adding 4-methylbenzenesulfonic acid as catalyst, but the expected products were still not obtained. Compounds 3 and 4 were finally obtained in 69.6% and 25.1% yield, respectively, by using activated alkaline aluminum oxide as dehydrating agent and anhydrous toluene as solvent.

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