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Asymmetric Michael Addition Catalyzed by Aluminum Lithium Bis-(*R*)-binaphthoxide*

K. Tabatabaeian, M. Mamaghani, and A. Pourahamad

Chemistry Department, Faculty of Science, Guilan University, P.O.Box 1914, Rasht, Iran
e-mail: taba@cd.gu.ac.ir

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Abstract—Enantiomerically pure aluminum lithium bis-(*R*)-binaphthoxide [(*R*)-ALB] was synthesized and used to catalyze asymmetric Michael addition of diethyl malonate to ethyl crotonate.

One of the most fascinating aspects of modern organic chemistry is the synthesis of optically active chiral compounds which play an important role in medicine, agriculture, food industry, and manufacture of liquid crystals [1]. Among methods available for preparing such compounds, catalytic asymmetric synthesis has attracted the most attention. Although catalytic antibodies or structurally modified enzymes are now becoming accessible [2], molecular catalysts (in particular homogeneous) have a great advantage because their structures can be modified to improve their efficiency.

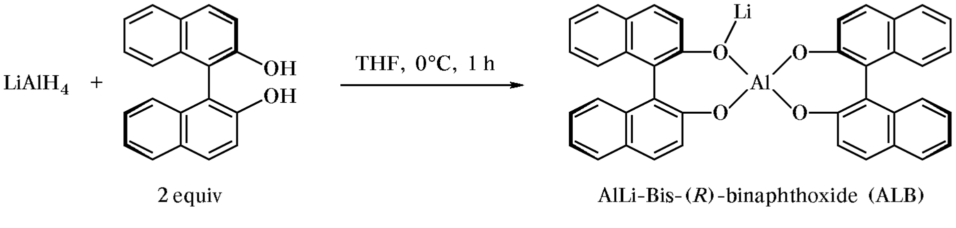
Many catalytic asymmetric syntheses with organometallic compounds have been carried out [3]. The respective characteristics, chemical reactivities and Lewis acidities, play crucial role in the key steps. The use of amphoteric $Zr(OBu\text{-}t)_4$ for developing a new class of basic asymmetric catalysts [4] led to the development of exciting heterobimetallic asymmetric catalysts with conceptually new chemical reactivities [5]. Heterobimetallic asymmetric catalysts efficiently promote a number of reactions through the synergistic cooperation between two different metals and a chiral template in a manner analogous to that observed in enzymatic processes involving metal ion cocatalysis [5].

Chiral bidentate ligands based on the 1,1′-binaphthalene system have achieved remarkable success in asymmetric synthesis, ensuring in many cases a high enantioselectivity (>90%) [6]. This success has focused on a more convenient synthesis of the homochiral 1,1′-binaphthalene-2,2′-diol (BINOL) ligand and a chiral building block for preparation of atropoisomeric chiral molecules possessing a C_2 axis of symmetry.

The present communication describes the development of the use of heterobimetallic asymmetric catalyst, namely aluminum lithium bis-(*R*)-binaphthoxide [(*R*)-ALB], in a new asymmetric Michael reaction (Scheme 1). For this purpose, racemic 1,1′-binaphthalene-2,2′-diol was synthesized [7] and resolved by L-proline [8]. The procedure was repeated several times until a high optical purity (ee > 97%) was achieved. The ligand thus obtained was used in the preparation of (*R*)-ALB.

In order to extend the catalytic application of (*R*)-ALB, asymmetric Micheal addition of diethyl malonate to ethyl crotonate was accomplished in

Scheme 1.



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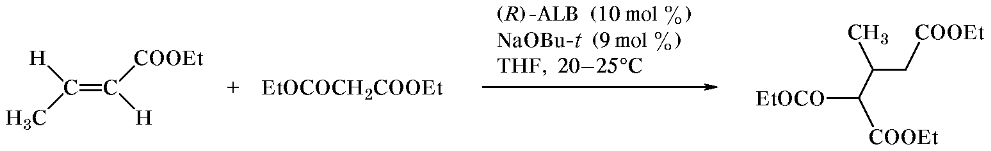
* The original article was submitted in English.

Scheme 2.



accordance with Scheme 2. The addition product was isolated in 70% yield as a dense oil, $[\alpha]_D^{26}$ = 15° (*c* = 1, $CHCl_3$). It was analytically pure (according to the GLC and ^1H NMR data).

The results of the present work provide further insight to the extension of studies initiated by Shibasaki and co-workers [9] on the use of heterobimetallic catalysts in asymmetric synthesis and encourage more research in this field.

EXPERIMENTAL

The IR spectra were recorded on a Shimadzu 470 spectrometer. The ^1H NMR spectra were obtained on a Bruker instrument operating at 80 MHz in the Fourier transform mode; tetramethylsilane was used as internal reference. GLC analysis was performed on a Buck Scientific 910 instrument. The mass spectra were run on a Sisons Trio-1000 mass spectrometer coupled with a Sisons 8000 gas chromatograph. The optical rotations were measured on a Polax-Atago polarimeter (cell length 10 cm). The melting points were determined using an Electrothermal instrument and are incorrected. Silica gel 60 GF_{254} (Merck) was used for column chromatography. The solvents were dried by standard methods prior to use.

Preparation of aluminum lithium bis-(*R*)-binaphthoxide [(*R*)-ALB] [9]. To a suspension of 94.9 mg (2.5 mmol) of $LiAlH_4$ in 10 ml of anhydrous tetrahydrofuran at 0°C we added a solution of 1.43 g (5 mmol) of optically pure (>97%) (*R*)-BINOL in 10 ml of anhydrous tetrahydrofuran, and the mixture was stirred for 0.5 h at 0°C and for 1 h at 25°C. It was then left overnight under dry argon, and the resulting colorless solution was used as a 0.1 M solution of (*R*)-ALB.

Michael addition of diethyl malonate to ethyl crotonate, catalyzed by (*R*)-ALB. To a 0.1 M solution of (*R*)-ALB (5 ml) containing 0.57 g (5 mmol) of ethyl crotonate, 0.8 g (5 mmol) of diethyl malonate, and 0.04 ml (0.45 mmol) of NaOBu-*t* we added with stirring at 0°C 0.9 equiv of (*R*)-ALB. The mixture was stirred for 3 days at room temperature, and the reaction was stopped by adding 20 ml of 1 N hydrochloric acid. The product was extracted into ethyl acetate (3 × 100 ml), and the organic phase was washed with a solution of sodium carbonate and dried over anhydrous sodium sulfate. The solvent was removed on a rotary evaporator, and the residue was purified by column chromatography on silica gel using petroleum ether–ethyl acetate (4 : 1) as eluent. We isolated 0.96 g (3.5 mmol, 70%) of the target Michael adduct as a dense oil, $[\alpha]_D^{26}$ = 15° (*c* = 1, $CHCl_3$). IR spectrum (neat), ν, cm^{-1}: 2950, 1730, 1300–1000. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1 d (3H, CH_3, *J* = 5.6 Hz), 1.15 m (9H, $OCH_2C\mathbf{H}_3$, *J* = 5.1 Hz), 2.1–2.7 m (3H, $CHCH_2$), 3.3 d (1H, CH, *J* = 6.1 Hz), 4.1 m (6H, $OC\mathbf{H}_2CH_3$). Mass spectrum, *m*/*z* (I_{rel}, %): 229 (9.3) $[M-OEt]^+$, 201 (24.4), 187 (52), 183 (100), 139 (12.6), 115 (30.7), 87 (59.8), 73 (25.6), 45 (33.45), 42 (35).

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