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Convenient Preparation of Chiral *trans*-9,10-Dihydrophenanthrene-9,10-diamine

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Abstract: Chiral *trans*-9,10-dihydrophenanthrene-9,10-diamine was conveniently prepared from biphenyl-2,2′-dialdehyde using intramolecular imino pinacol coupling and oxidative cleavage of aminoalcohol as key steps.

Keywords: *trans*-9,10-Dihydrophenanthrene-9,10-diamine, imino pinacol coupling, oxidative cleavage, salen, vicinal diamine

INTRODUCTION

The vicinal diamines have found widespread applications in asymmetric synthesis.[1] Among them, *trans*-1,2-diaminocyclehexane **1** and *trans*-1,2-diphenyl-ethylenediamine **2** (Scheme 1) represent two successful examples whose derivatives are widely employed as chiral ligands as well as organocatalysts.[2–5] Therefore, we were interested in exploring the synthesis and the properties of chiral *trans*-9,10-dihydrophenanthrene-9,10-diamine (Scheme 1, **3**), a structural hybrid of vicinal diamines **1** and **2**.

Substituted chiral *trans*-9,10-dihydrophenanthrene-9,10-diamines ($R \neq H$) have been synthesized[6–9] and employed as chiral ligands in enantioselective Diel–Alder reactions.[9] In this article, we report our synthesis of free chiral diamine **3** (R=R'=H).

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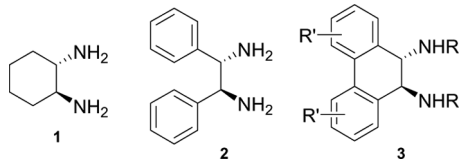
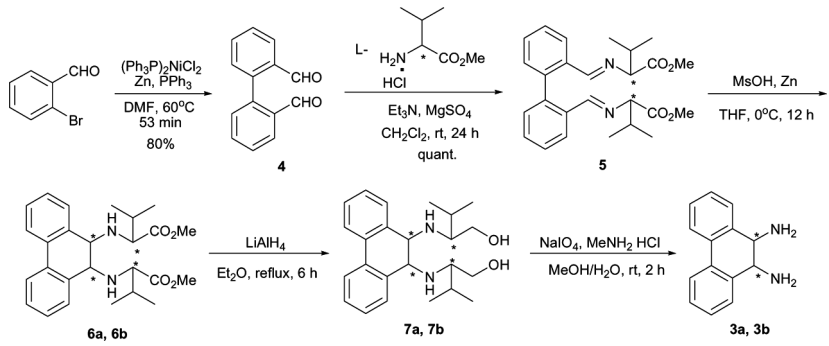


Scheme 1. Structures of vicinal diamines.

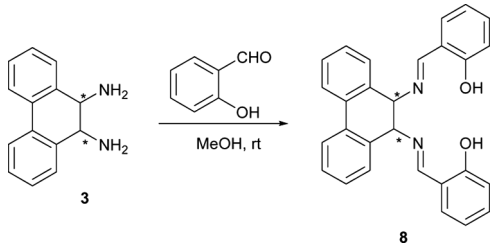
RESULTS AND DISCUSSION

The synthetic approaches of chiral *trans*-9,10-dihydrophenanthrene-9,10-diamine are outlined in Scheme 2.

Biphenyl-2,2′-dialdehyde **4** was easily obtained through an Ullmann reaction of 2-bromobenzaldehyde.[10] The formation of amino acid–derived Schiff's base **5** brought amino groups and chirality into the substrate. Then, the 9,10-dihydrophenanthrene-9,10-diamine structure was constructed by a intramolecular imino pinacol coupling to give diamino diester diastereomer mixture **6**, which was separated by column chromatography to give two *trans*-diamino diesters **6a** and **6b** with 40.0% yield and 13.5% yield respectively. No *cis*-diamines were obtained in our synthesis. After a failed attempt to obtain the target diamine **3** using Kise's one-pot $Pb(OAc)_4$ cleavage method,[11] we converted the diamino diesters **6a** and **6b** to diamino dialcohols **7a** and **7b**, which were then deprotected by the oxidation of $NaIO_4$ to form the target diamines **3a** and **3b**. In the oxidation cleavage step, no reaction occurred in the absence of $MeNH_2{\cdot}HCl$. However, use of $HIO_4{\cdot}2H_2O$ as an oxidant led to no diamine product.



Scheme 2. Synthetic approaches of chiral *trans*-9,10-dihydrophenanthrene-9,10-diamine.



Scheme 3. Preparation of salen-type Schiff's base.

Thus, the two enantiomers of chiral unsubstituted *trans*-9,10-dihydrophenanthrene-9,10-diamine can be conveniently prepared. However, this diamine quickly degenerates in solution. We then converted it to its salen-type Schiff's base **8** (Scheme 3) as a stable derivative immediately after its separation from the reaction mixture of the deprotection step.

In summary, we have developed a convenient method to prepare the two enantiomers of chiral *trans*-9,10-dihydrophenanthrene-9,10-diamine. In contrast with the previous methods to synthesize this type of compounds,[6,8,9] no chiral biaryl dialdehydes are needed in our method. This method would be expected to be employed in the synthesis of other vicinal diamines. The determination of the absolute configurations and further investigation of their properties and applications in asymmetric synthesis are still in process.

EXPERIMENTAL

All reactions were conducted in oven-dried glassware. NMR spectra were measured on a Bruker 300-MHz spectrometer. Chemical shifts were reported in parts per million (ppm) relative to internal tetramethylsilane (TMS). Column chromatography was carried out on silica gel (200–400 mesh) using petroleum ether (60–90°C) and EtOAc as eluents.

Diimine Diester (5)

A solution of biphenyl-2,2′-dialdehyde (500 mg, 2.4 mmol), L-valine methyl ester hydrochloride (797 mg, 4.8 mmol), and 0.70 ml Et_3N (5.0 mmol) in 20 ml CH_2Cl_2 was stirred with 2 g $MgSO_4$ at room temperature for 24 h. After filtration, the filtrate was washed with saturated aqueous $NaHCO_3$ and dried over anhydrous $MgSO_4$ to give 1.04 g of yellow viscous oil as a crude product with quantitative yield.

Diamino Diesters (6a and 6b)

In an ice bath, the diimine diester crude product **5** was dissolved in 50 ml freshly distilled THF, stirred with 1.6 g zinc powder (24 mmol) in an N_2 atmosphere. Methanesulfonic acid (MsOH) (1.6 ml, 26 mmol) was added at this temperature. After stirring at 0°C for 12 h, the reaction was stopped with saturated $NaHCO_3$, filtered, and extracted with CH_2Cl_2. The organic phases were combined, dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was separated by column chromatography to give two diastereomers of *trans*-diamino diesters **6a** and **6b**.

Compound **6a**

Pale yellow viscous oil, 417 mg, 40.0% yield. $[\alpha]_D^{26} = -95.7$ (c = 0.501, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): $\delta = 0.611$ (br, 12H), 1,67 (br, 4H), 2.95 (br, 2H), 3.73 (s, 8H), 7.24–7.29 (m, 4H), 7.33–7.38 (m, 2H), 7.76 (d, $J = 7.5$ Hz, 2H). ^{13}C NMR ($CDCl_3$): $\delta = 18.5$, 19.1, 31.6, 51.7, 60.5, 64.7, 124.2, 127.5, 131.0, 133.2, 134.9, 175.6.

Compound **6b** (Less Polar than **6a**)

Pale yellow viscous oil, 141 mg, 13.5% yield. $[\alpha]_D^{26} = +102.4$ (c = 0.502, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): $\delta = 0.71$ (d, $J = 6.9$ Hz, 6H), 0.77 (d, $J = 6.9$ Hz, 6H), 1.66–1.77 (m, 2H), 1.93 (br, 2H), 3.1 (d, $J = 6.0$ Hz, 2H), 3.48 (s, 6H), 3.71 (s, 2H), 7.22–7.24 (m, 4H), 7.31–7.36 (m, 2H), 7.78 (d, $J = 8.1$ Hz, 2H).^{13}C NMR ($CDCl_3$): $\delta = 18.5$, 19.2, 32.0, 51.3, 60.7, 65.5, 123.8, 127.7, 128.4, 130.5, 133.0, 136.0, 175.5.

Diamino Dialcohols (7a and 7b)

A solution of 100 mg diamino diester **6** (0.23 mmol) in 10 ml of diethyl ether was refluxed with excess $LiAlH_4$ for 6 h. After cooling to room temperature, the reaction was ceased by careful addition of 1 ml water. The ether solution was filtered, dried, and concentrated to give a colorless solid as product (87 mg, quant.)

Compound **7a**

Prepared from **6a**. White solid, mp 51–53°C. $[\alpha]_D^{26} = -89.5$ (c = 0.500, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): $\delta = 0.65$ (d, $J = 6.9$ Hz, 6H), 0.73 (d,

$J = 6.9$ Hz, 6H), 1.52–1.65 (m, 2H), 2.46–2.51 (m, 2H), 3.24 (dd, $J = 10.8$, 6.3 Hz, 2H), 3.59 (dd, $J = 11.4$, 4.2 Hz, 2H), 3.96 (s, 2H), 7.26–7.33 (m, 4H), 7.35–7.41 (m, 2H), 7.81 (d, $J = 7.8$ Hz, 2H). ^{13}C NMR ($CDCl_3$): $\delta = 18.6$, 19.1, 59.6, 61.0, 61.7, 124.2, 128.0, 128.7, 130.5, 132.6, 135.8.

Compound **7b**

Prepared from **6b**. Colorless viscous oil. $[\alpha]_D^{26} = +115.9$ (c = 0.501, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): $\delta = 0.78$ (d, $J = 6.9$ Hz, 6H), 0.84 (d, $J = 6.9$ Hz, 6H), 1.63–1.81 (m, 2H), 1.91 (br, 2H), 2.46–2.52 (m, 2H), 3.23 (dd, $J = 10.5$, 6.0 Hz, 2H), 3.47 (dd, $J = 10.8$, 4.2 Hz, 2H), 3.94 (s, 2H), 7.25–7.29 (m, 4H), 7.33–7.41 (m, 2H), 7.79 (d, $J = 7.5$ Hz, 2H). ^{13}C NMR ($CDCl_3$): $\delta = 18.7$, 19.6, 29.4, 58.4, 61.0, 61.5, 124.4, 128.2, 128.8, 130.7, 132.7, 136.1.

Diamines (3a and 3b)

Diamino dialcohol **7** (100 mg, 0.26 mmol) was stirred in a solution of 3 ml MeOH and 1.5 ml H_2O. $NaIO_4$ (391 mg, 1.8 mmol) and $MeNH_2$·HCl (371 mg, 5.5 mmol) were added, and the reaction was monitored by TLC. When the diamino dialcohol completely disappeared (about 2 h), 3 ml of 3 M NaOH were added to cease the reaction. The mixture was filtered, and the filtrate was extracted three times with CH_2Cl_2. The CH_2Cl_2 phases were combined and concentrated to give a green solid as crude diamine product. ^{1}H NMR ($CDCl_3$): $\delta = 2.16$ (br, 4H), 3.89 (s, 2H), 7.28–7.40 (m, 4H), 7.47 (dd, $J = 6.9$, 1.2 Hz, 2H), 7.78 (d, $J = 7.8$ Hz, 2H). LC-MS 210.1.

Salen-Type Schiff's Bases (8a and 8b)

The crude diamine was stirred in 5 ml MeOH with excess freshly distilled salicylaldehyde for 1 h. After concentration, the residue was separated by column chromatography to give salen-type Schiff's base **8**.

Compound **8a**

Pale yellow solid, mp (decomp.) 73–75°C, $[\alpha]_D^{26} = -97.3$ (c = 1.02, CH_2Cl_2), 38 mg, 35.0% yield, two steps from diamino dialcohol **7a**. IR (KBr, cm^{-1}): 3440, 3068, 2923, 2853, 1635, 1578, 1494, 1460, 1451, 1275, 1069, 752. ^{1}H NMR ($CDCl_3$): $\delta = 4.80$ (s, 2H), 6.82 (t, $J = 7.5$ Hz,

Hz, 2H), 6.92 (d, $J = 8.4$ Hz, 2H), 7.19 (dd, $J = 7.8$, 1.5 Hz, 2H), 7.25–7.36 (m, 6H), 7.45 (td, $J = 7.5$, 1.2 Hz, 2H), 7.87 (d, $J = 7.8$ Hz, 2H), 8.36 (s, 2H), 13.0 (br, 2H). ^{13}C NMR ($CDCl_3$): $\delta = 72.2$, 117.0, 118.6, 119.0, 124.2, 127.1, 128.5, 128.8, 132.0, 132.9, 133.0, 134.7, 161.1, 168.0. HRMS calcd. for $C_{28}H_{22}N_2O_2$ (M^+) 418.1681; found 418.1680.

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