Using Natural Cinchona Alkaloids to Promote the Enantioselective Addition of Dialkylzinc to *N*-Diphenylphosphinylimines†

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Cinchona alkaloids are utilized as chiral ligands to promote the enantioselective addition of dialkylzinc to *N*-diphenylphosphinylimines affording enantiomerically enriched *N*-diphenylphosphinylamines in up to 91% *ee*.

Keywords cinchona alkaloids, dialkylzinc, *N*-diphenylphosphinylimines

Introduction

The natural chiral products are attractive and economical source for optically pure chiral agents.[1] It is an interesting and worthwhile project to directly employ natural molecules as chiral catalysts, ligands or auxilliaries. The importance of chiral amines has intrigued the hot development of new synthetic methodologies.[2-4] Dialkylzinc addition to imines in enantioselective manner, leading to chiral amines, has been examined by several groups.[5] Many chiral ligands have been developed for the diethylzinc addition to diphenylphosphinoylimines, but most of them suffer from inconveniences associated with their multistep-synthesis,[5e] which make them too expensive to compete with other families of chiral ligands, especially when stoichiometric amounts were used. Therefore, it is still valuable to search for easily accessible and economical chiral reagents for the dialkylzinc addition to imines.

In our previous work, we have reported the application of easily available amino alcohols **1** and chiral oxazolines **2** in the high enantioselective diethylzinc addition to diphenylphosphinylimines.[6] Those ligands have such common characteristics: chiral β-amino alcohol type ligands contain chiral carbon which both bonded to hydroxyl group and tethered to an aromatic ring. In addition, Andersson found that in the presence of stoichiometric amount of chiral bicyclic β-amino alcohols **3** with sterically constrained bicyclo [2.2.1] ring system, the title reaction gave high enantioselectivities.[5e]

The multifunctionality of the cinchona alkaloids may

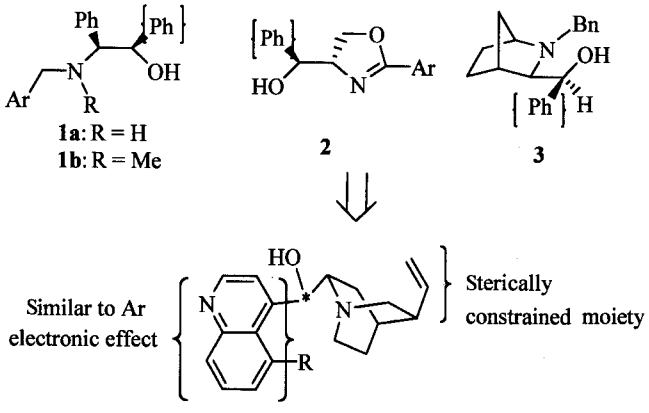

Fig. 1 Chiral β-amino alcohol type ligands.

be rather unique among the nature molecules.[1a] They contain aquinoline ring which should have similar electronic effect as that of aromatic ring. Their bicyclo [2.2.2] ring system with a conformationally restricted nitrogen may block the approach of the attacking species to one of the enantiotopic faces of the imines. Besides that, the hydroxyl group attached to the chiral carbon is obviously important for the face selectivity of the addition. So we anticipated that cinchona alkaloids would be good promoters for the enantioselective addition of dialkylzinc reagents to *N*-(diphenylphosphinoyl) imines because of their electronic and structurally rigid effects. Herein we report the results of our studies regarding cinchona alkaloids mediated asymmetric addition of alkylzincs to imines.

Results and discussion

The cinchonidine (**CD**), 10,11-dihydrocinchonidine (**HCD**) and quinidine (**QD**) were tested as promoters for the addition of dialkylzinc reagents to several *N*-diphenylphosphinylimines. As a general procedure, the dialkylzinc

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reagent (5 equiv.) was added to a stirred solution of the imine and the ligand (1 equiv.) in dry toluene under Ar at room temperature, and then the reaction was stirred for 16 h or 48 h. After quenching with aqueous 2 N HCl and usual workup, the expected products were obtained.

The results are summarized in Table 1. As we expected, cinchona alkaloids were efficient for the title reaction. It seemed that **QD** was better than **CD** in promoting the reaction. We presumed that the electron-donating methoxy group in **QD** made the resulting zinc complex more reactive. Compared with **CD**, ligand **HCD** resulted in a decrease in both isolated yield and enantioselectivity (Entry 2). The configuration of the product was controlled by the stereochemistry at C-9. When the chirality at C-9 of **CD** was *R* configuration, *R*-rich enantiomer product was obtained. While the chirality at C-9 of **QD** was *S* configuration, *S*-rich enantiomer was yielded. Imines **4e** and **4f** were shown less reactive than **4a** to accept the dialkylzinc attack (Table 1, Entries 11—13). The imines **4b** and **4c** possessing a benzene ring substituted by electron-donating groups such as OCH_3 and OCH_2O at the *para*- or *meta*-position, were proven to be good substrates for the reaction, which gave the corresponding adducts in 89% and 91% *ee*, respectively in the presence of stoichiometric amount of **QD** (Entries 5 and 7). Enantioselective butylation of **4c** with Bu_2Zn using 1 equiv. of ligand **QD** afforded the corresponding phosphoramide **5g** in 91% *ee* (Entry 8). It was the highest *ee* so far reported for the butylation of imines.

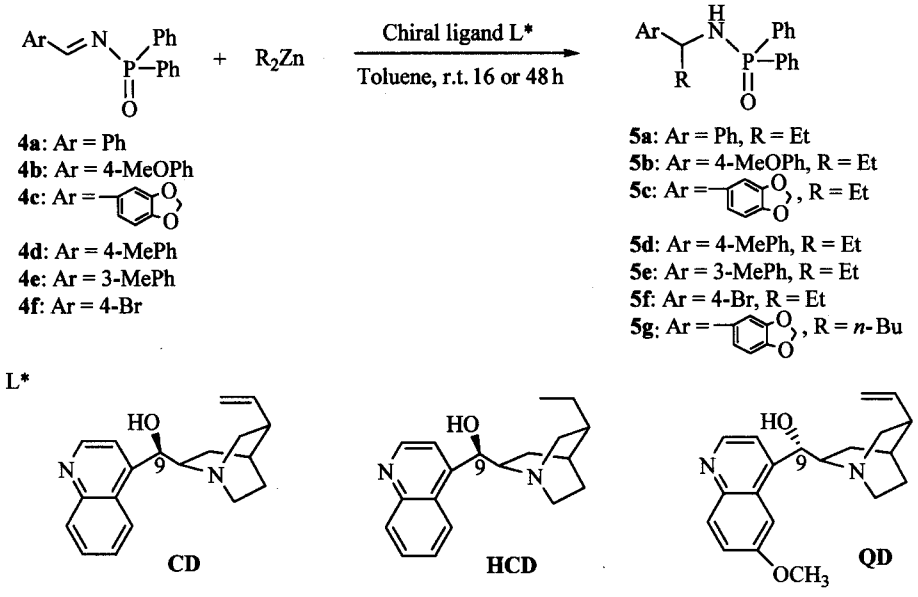

Fig. 2 Dialkylzinc addition to *N*-diphenylphosphinoyl imines mediated by **CD**, **HCD** and **QD**.

Table 1 Asymmetric dialkylzinc addition to *N*-diphenylphosphinoyl aromatic imines promoted by **CD**, **HCD** and **QD**[a]

Entry	Ar	Imine	R	Ligand	Time (h)	Yield[b] (%)	*ee*[c] (%)	Config.
1	Ph	**4a**	Et	**CD**	48	76	80	*R*
2	Ph	**4a**	Et	**HCD**	48	43	78	*R*
3	Ph	**4a**	Et	**QD**	48	82	85	*S*
4	4-MeOPh	**4b**	Et	**CD**	48	65	87	*R*
5	4-MeOPh	**4b**	Et	**QD**	16	67	89	*S*
6	Piperonyl	**4c**	Et	**CD**	48	85	87	*R*
7	Piperonyl	**4c**	Et	**QD**	16	80	91	*S*
8	Piperonyl	**4c**	*n*-Bu	**QD**	48	50	91	*S*
9	4-MePh	**4d**	Et	**CD**	48	79	84	*R*
10	4-MePh	**4d**	Et	**QD**	16	77	84	*S*
11	3-MePh	**4e**	Et	**CD**	48	62	75	*R*
12	3-MePh	**4e**	Et	**QD**	16	60	77	*S*
13	4-BrPh	**4f**	Et	**QD**	16	60	61	*S*

[a] The reaction was carried out at room temperature in the presence of stoichiometric amount of ligand for 16—48 h. [b] Isolated yields based on imines. [c] Determined on HPLC.

In summary, we have shown that natural molecules, cinchona alkaloids, are promising ligands for the asymmetric addition of dialkylzinc reagents to imines. Although the addition reaction is still performed using a full equivalent of the chiral ligand, it should be noted that natural cinchona alkaloids is very cheap, available and could be easily recovered during the work-up.

Experimental

General

NMR spectra were recorded on a Brucker-300 MHz spectrometer. Elemental analysis was carried out using Carlo Erba-1106 Analyzer. EI Mass spectra were recorded on VG-7070E instrument. IR spectra were recorded on Nicolet 200SXV FT-IR instrument. Optical rotation were recorded on PERKIN ELMER polarimeter 341 instrument. HPLC analysis was performed on Beckman chromatography (110B solvent Delivery Module, 168 variable wavelength detector). Chiralpak AD column was purchased from Daicel Chemical Industries, LTD. All reactions involving air and moisture sensitive were carried out under a dry argon atmosphere using standard Schlenk line techniques. Toluene was dried with sodium/benzophenone. Petroleum ether (PE) and ethyl acetate for column chromatography were distilled before use.

Materials

All starting materials were purchased from Acros and used directly. The *N*-diphenylphosphinoylimines **4a**, **4b**, **4c**, **4d**, **4e** and **4f** were prepared according to the method reported in the literature.[7-14] The **HCD** was prepared according to the method reported in the literature.[15]

Typical experimental procedure for the enantioselective addition of diethylzinc to n-diphenylphosphinoyl benzalimine (**4a**, 0.1 mmol) *in the presence of* **QD** (0.1 mmol)

Imine **4a** (30.5 mg, 0.1 mmol) and the **QD** (32.4 mg, 0.1 mmol) were suspended in toluene (2 mL) under argon. To the mixture was added Et_2Zn in hexane (1 mol/L, 0.5 mL, 0.5 mmol) at r.t.. After stirred for 16 or 48 h, the reaction was quenched with an aqueous solution of HCl (2 mol/L), and the aqueous layer was extracted with CH_2Cl_2. Then the **QD** was recovered by adding an aqueous solution of NaOH to the aqueous layer. The combined organic layer was washed with brine, and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by column chromatography on silica gel to give **5a**[5,6] as a white solid in 82% yield, m.p. 121—123 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.80 (t, J = 7.4 Hz, 3H, CH_3CH_2), 1.80—1.95 (m, 1H, CH_2CH_3), 1.98—2.10 (m, 1H, CH_2CH_3), 3.32 (m, 1H, NH), 4.10 (m, 1H, CHNH), 7.15—7.46 (m, 11H, ArH), 7.78—7.89 (m, 4H, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 10.5 (CH_3), 32.5 (CH_2), 57.1 (CHNH), 125.0 (Ar), 126.4 (Ar), 126.6 (Ar), 127.0 (Ar), 128.1 (Ar), 128.3 (Ar), 128.4 (Ar), 128.5 (Ar), 131.6 (Ar), 131.7 (Ar), 131.8 (Ar), 132.4 (Ar), 132.6 (Ar), 143.4 (Ar); IR (Nujol mull) ν: 3135 (NH), 1188 (P = O) cm^{-1}; MS (CI) m/z (%): 334 (M − H)$^+$, 306 (M − CH_2CH_3)$^+$, 258 (M − Ph)$^+$, 216 (Ph_2PONH^+), 201 (Ph_2PO^+). The enantiomeric excess of the major *S*-isomer was determined by HPLC (CHIRALPAK AD column, V (hexane) : V (propan-2-ol) = 80:20; flow rate 1 mL/min; *R*-isomer, t_R 8.66 min and *S*-isomer, t_R 11.60 min) to be 85%.

N-[1-(4-*Methoxyphenyl*)*propyl*]-*P*, *P*-*diphenylphosphinoylamide* (**5b**) This compound[5g] was obtained as a white solid in 67% yield. m.p. 130—131 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.78 (t, J = 7.4 Hz, 3H, CH_3CH_2), 1.77—1.86 (m, 1H, CH_2CH_3), 1.96—2.05 (m, 1H, CH_2CH_3), 3.31 (m, 1H, NH), 3.81 (s, 3H, CH_3O), 4.04—4.07 (m, 1H, CHNH), 6.83 (d, J = 8.7 Hz, 2H, ArH), 7.09 (d, J = 8.7 Hz, 2H, ArH), 7.28—7.48 (m, 6H, ArH), 7.79—7.88 (m, 4H, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 10.6 (CH_3), 32.3 (CH_2), 55.2 (CH_3O), 56.6 (CHNH), 113.7 (Ar), 127.5 (Ar), 128.1 (Ar), 128.2 (Ar), 128.3 (Ar), 128.5 (Ar), 131.6 (Ar), 131.7 (Ar), 131.8 (Ar), 132.4 (Ar), 132.6 (Ar), 135.5 (Ar), 158.4 (Ar); IR (Nujol mull) ν: 3203 (NH), 1182 (P = O) cm^{-1}; MS (CI) m/z (%): 365 (M$^+$), 336 (M − CH_2CH_3)$^+$, 201 (Ph_2PO^+), 164 (M − Ph_2PO)$^+$. The enantiomeric excess of the major *S*-isomer was determined by HPLC (Chiralpak AD column, V (hexane) : V (propan-2-ol) = 80:20; flow rate 1 mL/ min; *R*-isomer, t_R 8.02 min and *S*-isomer, t_R 9.54 min) to be 89%.

N-*Piperonylpropyl*-*P*, *P*-*diphenylphosphinamide* (**5c**) This compound was obtained as a white solid in 80% yield. m.p. 154—155 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 6.08—6.09 (m, 2H, OCH_2O), 6.90—6.96 (m, 1H, ArH), 7.35—7.63 (m, 8H, ArH), 7.90—7.97 (m, 4H, ArH), 9.18 (d, $J_{H\text{-}P}$ = 33.0 Hz, 1H, CH = N); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 101.9 (OCH_2O), 106.8 (Ar), 107.2 (Ar), 108.3 (Ar), 128.3 (Ar), 128.4 (Ar), 128.5 (Ar), 128.6 (Ar), 128.8 (Ar), 130.7 (Ar), 131.0 (Ar), 131.4 (Ar), 131.5 (Ar), 131.6 (Ar), 131.8 (Ar), 132.3 (Ar), 133.9 (Ar), 148.5 (Ar), 152.5 (Ar), 171.8 (C = N); IR (Nujol mull) ν: 1616 (C = N), 1270 (C—O), 1200 (P = O) cm^{-1}; MS (CI) m/z (%): 349 (M$^+$), 272 (M − Ph)$^+$, 202 (Ph_2POH^+), 201 (Ph_2PO^+). The enantiomeric excess of the major *S*-isomer was determined by HPLC (Chiralpak AD column, V (hexane): V (propan-2-ol) = 80:20; flow rate 1 mL/ min; *R*-isomer, t_R 7.94 min and *S*-isomer, t_R 11.50 min) to be 91%.

N-[1-(4-*Methylphenyl*)*propyl*]-*P*, *P*-*diphenylphosphinoylamide* (**5d**) This compound[5g] was obtained as a white solid in 77% yield. m.p. 107—110 ℃; ^{1}H NMR

($CDCl_3$, 300 MHz) δ: 0.78 (t, J = 7.4 Hz, 3H, CH_3CH_2), 1.78—1.90 (m, 1H, CH_2CH_3), 1.95—2.09 (m, 1H, CH_2CH_3), 2.35 (CH_3Ar), 3.30—3.33 (m, 1H, NH), 4.05—4.14 (m, 1H, CHNH), 7.06 (d, J = 8.1 Hz, 2H, ArH), 7.12 (d, J = 8.1 Hz, 2H, ArH), 7.35—7.48 (m, 6H, ArH), 7.75—7.89 (m, 4H, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 10.5 (CH_3), 21.0 (CH_3Ar), 32.4 (CH_2), 56.9 (CHNH), 126.3 (Ar), 128.1 (Ar), 128.3 (Ar), 128.4 (Ar), 129.1 (Ar), 131.6 (Ar), 131.7 (Ar), 131.8 (Ar), 132.4 (Ar), 132.5 (Ar), 132.6 (Ar), 136.6 (Ar), 140.4 (Ar); IR (Nujol mull) ν: 3224 (NH), 1185 (P = O) cm^{-1}; MS (CI) m/z (%): 320 $(M - CH_2CH_3)^+$, 201 (Ph_2PO^+), 148 $(M - Ph_2PO)^+$. The enantiomeric excess of the major S-isomer was determined by HPLC (Chiralpak AD column, V (hexane) : V (propan-2-ol) = 92 : 8; flow rate 1 mL/ min; R-isomer, t_R 6.60 min and S-isomer, t_R 7.62 min) to be 84%.

N-[1-(3-*Methylphenyl*)*propyl*]-*P*, *P*-*diphenylphosphinamide* (**5e**) This compound was obtained as a white solid in 60% yield. m.p. 116—118 ℃; ^1H NMR ($CDCl_3$, 300 MHz) δ: 2.45 (s, 3H, CH_3Ar), 7.40—7.51 (m, 8H, ArH), 7.69—7.99 (m, 6H, ArH), 9.30 (d, $J_{H\text{-}P}$ = 33.0 Hz, 1H, CH = N), ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 21.2 (CH_3Ar), 127.8 (Ar), 128.3 (Ar), 128.5 (Ar), 128.7 (Ar), 130.2 (Ar), 131.4 (Ar), 131.6 (Ar), 131.7 (Ar), 131.8 (Ar), 132.1 (Ar), 133.7 (Ar), 134.5 (Ar), 138.7 (Ar), 173.8 (C = N), 173.9 (C = N); IR (Nujol mull) ν: 1628 (C = N), 1200 (P = O) cm^{-1}; MS (CI) m/z (%): 319 (M^+), 242 (M - Ph)$^+$, 216 (Ph_2PONH^+), 202 (Ph_2POH^+), 201 (Ph_2PO^+). The enantiomeric excess of the major S-isomer was determined by HPLC (Chiralpak AD column, V (hexane) : V (propan-2-ol) = 90 : 10; flow rate 1 mL/ min; R-isomer, t_R 5.04 min and S-isomer, t_R 7.26 min) to be 77%.

N-[1-(4-*Bromophenyl*)*propyl*]-*P*, *P*-*diphenylphosphinamide* (**5f**) This compound[5g] was obtained as a white solid in 60% yield. m.p. 174—176 ℃; ^1H NMR ($CDCl_3$, 300 MHz) δ: 0.78 (t, J = 7.2 Hz, 3H, CH_3CH_2), 1.74—1.84 (m, 1H, CH_2CH_3), 1.86—2.01 (m, 1H, CH_2CH_3), 3.38 (m, 1H, NH), 4.05 (m, 1H, CHNH), 7.03 (d, J = 7.8 Hz, 2H, ArH), 7.27—7.48 (m, 8H, ArH), 7.70—7.74 (m, 2H, ArH), 7.83—7.89 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 10.5 (CH_3), 32.3 (CH_2), 56.5 (CHNH), 120.7 (Ar), 128.2 (Ar), 128.3 (Ar), 128.5 (Ar), 130.8 (Ar), 131.4 (Ar), 131.7 (Ar), 131.8 (Ar), 132.3 (Ar), 132.4 (Ar), 132.5 (Ar), 133.5 (Ar), 142.5 (Ar), 142.6 (Ar); IR (Nujol mull) ν: 3224 (NH), 1184 (P = O) cm^{-1}; MS (EI) m/z (%): 415 (M^+), 385 ($M - CH_2 = CH_2$)$^+$, 305 ($M - Br - CH_2CH_3$)$^+$, 212 ($M - Ph_2PO$)$^+$, 201 (Ph_2PO^+). Anal. calcd for $C_{21}H_{21}BrNOP$: C 60.88, H 5.11, N 3.38, Br 19.29; found C 60.97, H 5.16, N 3.53, Br 19.15. The enantiomeric excess of the major S-isomer was determined by HPLC (Chiralpak AD column, V (hexane) : V (propan-2-ol) = 90 : 10; flow rate 1 mL/ min; R-isomer, t_R 8.23 min and S-isomer, t_R 9.12 min) to be 61%.

N-*Piperonylpentyl*-*P*, *P*-*diphenylphosphinamide* (**5g**) This compound was obtained as a white solid in 50% yield. m.p. 159.1—159.3℃; ^1H NMR ($CDCl_3$, 300 MHz) δ: 0.80 (t, 3H, CH_3), 1.09—1.43 (m, 5H, $2CH_2$), 1.71—2.00 (m, 2H, CH_2CH), 3.17—3.29 (s,br, 2H, OCH_2O), 4.06 (d, 1H, NH), 6.55—6.70 (m, 3H, PhH), 7.27—7.87 (m, 10H, PhH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 13.8 (CH_3), 22.2 (CH_2), 28.2 (CH_2), 39.4 (CH_2), 55.6 (CH), 100.8 (OCH_2O), 106.6, 107.9 (ArC), 119.9 (ArC), 127.6 (ArC), 128.4 (ArC), 131.2 (ArC), 131.6 (ArC), 131.8 (ArC), 132.4 (ArC), 132.5 (ArC), 132.9 (ArC), 137.8 (ArC), 146.3 (ArC), 147.6 (ArC); MS (EI) m/z (%): 408 (M + 1), 350 [$(M - C_4H_9)^+$, 65], 206 [$(M + 1)^+ - Ph_2PO$, 100], 201 (Ph_2PO^+, 70). The enantiomeric excess of the major S-isomer was determined by HPLC (Chiralpak AD column, V (hexane) : V (propan-2-ol) = 90 : 10; flow rate 1 mL/ min; R-isomer, t_R 4.81 min and S-isomer, t_R 6.04 min) to be 91%.

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