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Resolution of enantiomers of [α-hydroxy-(*o*-chlorophenyl)methyl]phosphinic acid via diastereomeric salt formation with enantiopure 1-phenylethylamines

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ABSTRACT

The resolution of racemic α-hydroxy-H-phosphinic acid with enantiopure 1-phenylethylamines via diastereomeric salt formation was investigated. X-Ray crystallographic analysis of the salt revealed that (*R*)-1-phenylethylamine to be efficient resolving agent for obtaining a single enantiomer of [α-hydroxy-(*o*-chlorophenyl)methyl]phosphinic acid. Resolving racemic α-hydroxy-H-phosphinic acid with (*S*)-2-phenylethylamine also gave access to (*S*)-α-hydroxyalkylphosphinic acid in good yield.

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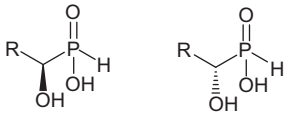
1. Introduction

α-Functionalized phosphinic acids have received considerable attention in medicinal chemistry and related fields.[1–3] Amongst the α-functional phosphinic acids, α-hydroxyalkylphosphinic acid derivatives have potential biological activities, such as enzyme and metalloenzyme inhibitors, bone resorption inhibitors, or as anti-viral, anti-tumoral and anti-bacterial agents, or fungicides.[4–6] Some chiral α-hydroxyphosphinic acids are useful intermediates for α-hydroxyphosphinyl peptides showing good inhibitory activity against renin.[7] In addition, the structure of the phosphinic functional group mimics the transition state of peptide hydrolysis and the symmetric nature of the phosphinic acid derivatives are expected to benefit from their binding to the homodimer of HIV-protease having a C_2-axis of symmetry.[8] Indeed, α-hydroxy-H-phosphinic acid derivatives are also used as extractants for the recovery or separation of certain metal ions.[9] In contrast to the wide range of literature studied for the separation α-hydroxyalkylphosphonic acid derivatives,[10] very little investigation has been carried out for the chiral separation of this class of compounds.[11] Kielbasinski et al. have reported the lipase-catalyzed kinetic resolution for a chiral hydroxymethylphosphinate possessing an asymmetric center at the phosphorus atom.[11a,b] The kinetic resolution of α-hydroxy(phenyl)-phosphinates containing two stereogenic centers at the phosphorus and the α-carbon atom through a lipase-catalyzed acylation has been reported by Shioji et al.[11c] Yokomatsu and co-workers have reported a novel chiral synthesis and separation of α-hydroxy-H-phosphinates with two stereogenic centers via lipase-catalyzed hydrolysis reactions of the corresponding racemic acetates.[11d] Although there is evidence that 1-hydroxy-H-phosphinic acids are pharmaceutically active,[12] to the best our knowledge, there are no reports in the literature for the separation of chiral α-hydroxy-H-phosphinic acids **1** using chiral resolving agents (Scheme 1).



(*R*)-**1** (*S*)-**1**

Scheme 1.

As a part of our ongoing efforts toward the synthesis and separation of diastereoisomers of α-functionalized phosphinic acids,[13] we have recently described a new method for the synthesis[14] and separation of diastereoisomeric and enantiomeric bis(α-hydroxyalkyl)phosphinic acids.[15] Herein we report the first resolution of (±)-α-hydroxy-H-phosphinic acids **1** via diastereomeric salt formation with enantiopure 1-phenylethylamines.

2. Results and discussion

Racemic (±)-α-hydroxy-H-phosphinic acids **1** were obtained in multi-gram quantities (45–63% isolated yields, Scheme 2) from the reaction of an aromatic aldehyde and hypophosphorus acid at reflux in ethanol for 48 h, according to a literature procedure (Scheme 2).[16] In an effort to resolve *rac*-**1**, we examined diastereomeric salt formation with one equivalent of (*R*)-2-phenylethylamine in a variety of solvents while expecting one of diastereomeric salts **2** or **3** to be preferably crystallized (Scheme 3). The ^{31}P NMR spectrum was used to determine the purity of the separable diastereomeric salts **2** and **3**. The ^{31}P NMR spectrum of the mixtures of crystallized salts of **2a–c** and **3a–c** exhibited no resolvable peaks. We were pleased to find that when *rac*-**1d** was treated with (*R*)-2-phenylethylamine in EtOH at reflux, the ^{31}P NMR spectra of the mixture of the crystallized salts **2d** and **3d** exhibited two singlet peaks at 19.04 and 19.11 ppm. Salt

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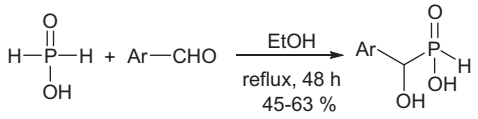


1

Ar (isolated yield %): **1a**) Ph (52%), **1b**) *p*-ClC_6H_4 (48%), **1c**) *m*-BrC_6H_4 (45%), **1d**) *o*-ClC_6H_4 (63%)

Scheme 2.

3d was found to precipitate from ethanol in a 32% yield at ambient temperature. The ^{31}P NMR spectrum of the crystallized salt **3d** exhibited a singlet at δ 19.11 ppm. The diastereomeric purity of salt **3d** can be readily assessed by ^{31}P NMR spectroscopy. In this case, salt **3d** is produced with >98% purity. The selection of the (*R*)-hand of *rac*-**1d** with (*R*)-1-phenylethylamine was confirmed by X-ray crystallography (Fig. 1) after recrystallisation. Since it is difficult to precisely determine the absolute structure by purely crystallographic methods, the known chirality of the (*R*)-1-phenylethylamine moiety was used as an internal reference. Treatment of salt **3d** with concd HCl gave enantiopure (*R*)-**1d** in a quantitative yield (Scheme 4). It should be noted that salt **2d** was found to precipitate out of the residue from ethanol in a 33% yield at ambient temperature. The ^{31}P NMR spectrum of the crystallized salt **2d** exhibited a singlet at δ 19.04 ppm. Treatment of salt **2d** with concd HCl gave enantiopure (*S*)-**1d** in a quantitative yield.

Resolving *rac*-**1d** with (*S*)-1-phenylethylamine in EtOH by the same procedure as described above, gave access to (*S*)-**1d** in a 30% yield (Scheme 4).

It is noteworthy that while other solvents, such as methanol and its mixtures with water were not suitable for obtaining good crystals due to excessive solubility of the intended salt in the solvents, good crystals of diastereomeric salts **2d** and **3d** could be prepared in 2-propanol. However both the diastereomeric salts **2d** and **3d** were found to precipitate more quickly from ethanol at ambient temperature.

Since 1-phenylethylamine is readily available in both enantiomeric forms, the resolution procedure above gives access to both enantiomers of (±)-α-hydroxy-H-phosphinic acids **1**.

3. Conclusion

We have shown that enantiomerically pure α-hydroxy-H-phosphinic acids **1** can be accessed via fractional crystallization of the salts formed from racemic (±)-α-hydroxy-H-phosphinic acids **1** and enantiopure 1-phenylethylamine. The present resolution method could open up the possibility to prepare optically active α-hydroxy-H-phosphinic acid derivatives with biological activity.

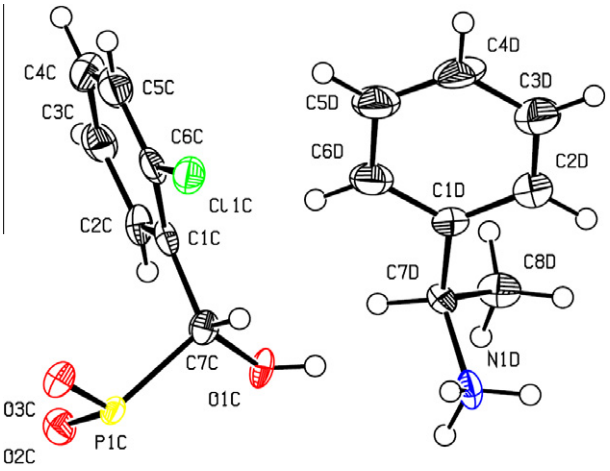


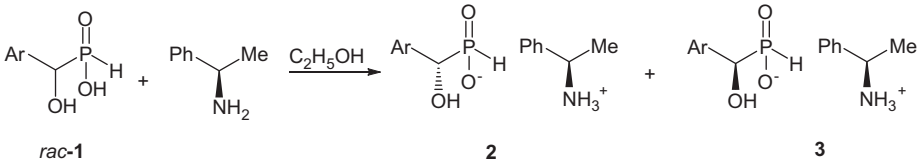
Figure 1. ORTEP drawing (*R*)-1-phenylethanaminium (*R*)-[α-hydroxy-(*o*-chlorophenyl)methyl]phosphinate (*R*,*R*)-**3d**.

4. Experimental

4.1. Materials and methods

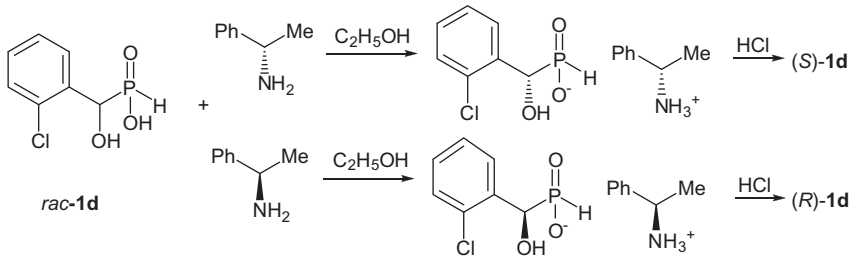
All chemicals were commercial products and distilled or recrystallized before use. All melting points were obtained by a Buchi 510 and are uncorrected. Optical rotations were recorded on a Perkin-Elmer 341 with a path length of 0.1 dm using the 589.3 nm D-line of sodium. Solutions were prepared using spectroscopic grade solvents and concentrations (*c*) are quoted in g/100 mL. The infrared (IR) spectra were determined using an FT-IR Brucker-Vector 22. NMR spectra were taken with a 400 Brucker Avance instrument with the chemical shifts being reported as δ ppm and couplings expressed in Hertz. Silica gel column chromatography was carried out with Silica gel 100 (Merck No. 10184).

X-Ray crystal data of **3d** were collected by a Bruker SMART APEX II diffractometer. The structure was solved by a direct method using



rac-**1** **2** **3**

Scheme 3.



rac-**1d** **3d**

Scheme 4.

SHLEXS-97 (Scheldrik, 1997) and refined with a full matrix laser-squares method. Molecular formula = $C_{15}H_{19}NClO_3P$, MW = 327.73, monoclinic, space group = $P2_1$, a = 7.0406(11) Å, b = 23.201(4) Å, c = 9.8854(15) Å, V = 1614.7(4) Å^3, T = 90 K, Z = 4, D_x = 1.348 mg/m^3, (Mo-Kα) = 0.71073 Å, R = 0.0426 over independent reflections. Crystallographic data (excluding structure factors) for the X-ray crystal structure analysis reported in this paper have been deposited with the Cambridge Crystallographic Data Center (CCDC) as supplementary publication No. CCDC 838013, copies of these data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

4.2. (±)-α-Hydroxy-H-phosphinic acids 1

This compound was obtained according to a method reported in the literature.[15] The aldehyde (30 mmol) was added to a solution of hypophosphorus acid (30 mmol-anhydrous) in 100 mL of ethanol and the resulting solution was stirred for 48 h at reflux. The solvent was evaporated and chromatography on silica gel with MeOH/$CHCl_3$ (1:9 to 10/0)) gave the pure product in 48–63% isolated yields. All products gave satisfactory spectroscopic data in accordance with the assigned structures.

4.2.1. [α-Hydroxy-(phenyl)methyl]phosphinic acid 1a

White solid: mp 111–112 °C (methanol) [lit. mp 107–108 °C];[17] FT IR (KBr) ν_{max}: 3371, 3300–2200, 1639, 1191 (P═O), 981; ^{1}H NMR (CD_3SOCD_3-400 MHz): 4.77 (1H, d, J = 8.8 Hz), 6.76 (1H, d, $^1J_{HP}$ = 529 Hz), 6.10–7.0 (1H, br, OH), 7.20–7.50 (5H, m); ^{31}P NMR (CD_3SOCD_3/H_3PO_4-162.0 MHz): 28.36; ^{13}C NMR (CD_3SOCD_3-100.6 MHz): 72.0 (d, J_{PC} = 108 Hz), 127.5 (d, J_{PC} = 6.0 Hz), 127.7 (d, J_{PC} = 3.0 Hz), 128.3 (d, J_{PC} = 2.0 Hz) 138.1; HRMS calcd for $C_7H_9O_3PNa$ (MNa^+): 195.0187. Found: 195.0185.

4.2.2. [α-Hydroxy-(*p*-chlorophenyl)methyl]phosphinic acid 1b

White solid: mp 122–123 °C (methanol); FT IR (KBr) ν_{max}: 3285, 3300–2200, 1647, 1158 (P═O), 971; ^{1}H NMR (CD_3SOCD_3-400 MHz): 4.80 (1H, d, J = 8.8 Hz), 6.77 (1H, d, $^1J_{HP}$ = 540 Hz), 6.10–7.0 (1H, br, OH), 7.25–7.50 (4H, m); ^{31}P NMR (CD_3SOCD_3/H_3PO_4-162.0 MHz): 27.68; ^{13}C NMR (CD_3SOCD_3-100.6 MHz): 71.1 (d, J_{PC} = 107 Hz), 128.4 (d, J_{PC} = 2.0 Hz), 129.2 (d, J_{PC} = 5.0 Hz), 132.4, 137.1; HRMS calcd for $C_7H_8O_3ClPNa$ (MNa^+): 228.9797. Found: 228.9800.

4.2.3. [α-Hydroxy-(*m*-bromophenyl)methyl]phosphinic acid 1c

White solid: mp 100–101 °C (methanol); FT IR (KBr) ν_{max}: 3274, 3300–2200, 1577, 1163 (P═O), 961; ^{1}H NMR (CD_3SOCD_3-400 MHz): 4.82 (1H, d, J = 9.2 Hz), 6.80 (1H, d, $^1J_{HP}$ = 536 Hz), 6.10–7.0 (1H, br, OH), 7.25–7.80 (4H, m); ^{31}P NMR (CD_3SOCD_3/H_3PO_4-162.0 MHz): 27.51; ^{13}C NMR (CD_3SOCD_3-100.6 MHz): 71.1 (d, J_{PC} = 107 Hz), 121.8 (d, J_{PC} = 3.0 Hz), 126.5 (d, J_{PC} = 5.0 Hz), 130.0 (d, J_{PC} = 5.0 Hz), 130.6 (d, J_{PC} = 2.0 Hz), 140.9; HRMS calcd for $C_7H_9O_3BrP$ (MH^+): 250.9473. Found: 250.9473.

4.2.4. [α-Hydroxy-(*o*-chlorophenyl)methyl]phosphinic acid 1d

White solid: mp 169–170 °C (methanol); FT IR (KBr) ν_{max}: 3299, 3300–2200, 1163 (P═O), 1027; ^{1}H NMR (CD_3SOCD_3-400 MHz): 5.16 (1H, d, J = 10.0 Hz), 6.81 (1H, d, $^1J_{HP}$ = 536 Hz), 6.10–6.8 (1H, br, OH), 7.30–7.60 (4H, m); ^{31}P NMR (CD_3SOCD_3/H_3PO_4-162.0 MHz): 26.83; ^{13}C NMR (CD_3SOCD_3-100.6 MHz): 68.8 (d, J_{PC} = 109 Hz), 127.6 (d, J_{PC} = 3.0 Hz), 129.4 (d, J_{PC} = 2.0 Hz), 129.5 (d, J_{PC} = 3.0 Hz), 129.7 (d, J_{PC} = 5.0 Hz), 132.2 (d, J_{PC} = 6.0 Hz) 136.3; HRMS calcd for $C_7H_9O_3ClP$ (MH^+): 206.9978. Found: 206.9983.

4.3. (−)-(*R*)-[α-Hydroxy-(*o*-chlorophenyl)methyl]phosphinic acid 1d

Racemic [α-hydroxy-(*o*-chlorophenyl)methyl]phosphinic acid **1d** (1.0 g, 5 mmol) and (*R*)-1-phenylethylamine (0.64 mL, 5 mmol) were dissolved in refluxing ethanol (15 mL). After refluxing for 5 h heating was stopped, and the flask was left to gradually cool and then kept at ambient temperature for 3–4 days. The resulting white solid was collected by filtration, washed with ethanol (2 mL in total), and dried in vacuo. The crude product was recrystallised from ethanol to yield (*R*)-1-phenylethanaminium (*R*)-[α-hydroxy-(*o*-chlorophenyl)methyl]phosphinate (*R*,*R*)-**3d** in a 32% yield as a white crystalline solid: mp 158–159 °C (ethanol); $[\alpha]_D^{20} = -37.5$ (*c* 0.37, EtOH); ^{1}H NMR (CD_3SOCD_3-400 MHz): 1.45 (3H, d, J = 6.8 Hz), 3.20–3.60 (1H, br, –OH), 3.24 (1H, q, J = 6.8 Hz), 4.79 (1H, d, J = 10.0 Hz), 6.75 (1H, d, $^1J_{HP}$ = 526 Hz), 7.15–7.55 (9H, m), 8.60–8.80 (3H, br, $-NH_3$); ^{31}P NMR (CD_3SOCD_3/H_3PO_4-162.0 MHz): 19.11; ^{13}C NMR (CD_3SOCD_3-100.6 MHz): 21.4, 50.3, 71.0 (d, J_{PC} = 95.0 Hz), 126.9 (d, J_{PC} = 2.0 Hz), 127.2, 127.8 (d, J_{PC} = 5.0 Hz), 128.6, 128.9, 129.1, 129.2 (d, J_{PC} = 4.0 Hz), 131.9 (d, J_{PC} = 5.0 Hz) 139.9, 140.5. HRMS calcd for $C_{15}H_{19}NClO_3P$ (MH^+): 328.0869. Found: 328.0873. The salt (*R*,*R*)-**3d** (0.26 g, 0.8 mmol) was suspended in ethyl acetate (50 mL) and 5% aqueous HCl (50 mL) was added. The biphasic mixture was stirred rapidly until all of the solid had dissolved. The organic layer was separated and the aqueous layer was re-extracted with ethyl acetate (3 × 50 mL). The combined organic layers were washed with water (100 mL), dried over $MgSO_4$, and concentrated to give (*R*,*R*)-**1** (0.16 g, quantitative) as a white crystalline solid: mp 169–170 °C (ethanol); $[\alpha]_D^{20} = -32.2$ (*c* 0.87, EtOH). Other spectroscopic data were identical to those of *rac*-**1d**. FT IR (KBr) ν_{max}: 3299, 3300–2200, 1163 (P═O), 1027; ^{1}H NMR (CD_3SOCD_3-400 MHz): 5.16 (1H, d, J = 10.0 Hz), 6.81 (1H, d, $^1J_{HP}$ = 536 Hz), 6.10–6.8 (1H, br, OH), 7.30–7.60 (4H, m); ^{31}P NMR (CD_3SOCD_3/H_3PO_4-162.0 MHz): 26.83; ^{13}C NMR (CD_3SOCD_3-100.6 MHz): 68.8 (d, J_{PC} = 109 Hz), 127.6 (d, J_{PC} = 3.0 Hz), 129.4 (d, J_{PC} = 2.0 Hz), 129.5 (d, J_{PC} = 3.0 Hz), 129.7 (d, J_{PC} = 5.0 Hz), 132.2 (d, J_{PC} = 6.0 Hz) 136.3.

4.4. (+)-(*S*)-[α-Hydroxy-(*o*-chlorophenyl)methyl]phosphinic acid 1d

Salt (*S*,*R*)-**2d** was found to precipitate from ethanol in a 33% yield at ambient temperature via fractional crystallization of the residue from the separation step of (*R*,*R*)-**3d** (Section 4.3). The resulting white solid was collected by filtration, washed with ethanol (2 mL in total), and dried in vacuo. The crude product was recrystallised from ethanol to yield (*R*)-1-phenylethanaminium (*S*)-[α-hydroxy-(*o*-chlorophenyl)methyl]phosphinate (*S*,*R*)-**2d** in 33% yield as a white crystalline solid: mp 156–157 °C (ethanol); $[\alpha]_D^{20} = +38.4$ (*c* 0.36, EtOH); ^{31}P NMR (CD_3SOCD_3/H_3PO_4-162.0 MHz): 19.04;). Other spectroscopic data were identical to those of (*R*,*R*)-**3d**. Following the above procedure (*S*)-**1d** obtained from *ent*-**2d** as a white solid in a quantitative yield: $[\alpha]_D^{20} = +30.2$ (*c* 0.79, EtOH). Other spectroscopic data were identical to those of *rac*-**1d**.

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