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Stereoselective reduction of *N*-phthaloyl α-amino ketones: an expeditious new synthesis of non-racemic *threo*-α-amino epoxides

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Abstract

Enantiopure α-diazoketones derived from *N*-Pht amino acids have been converted to *threo*-α-amino epoxides via HBr treatment followed by a highly *syn*-selective reduction with LiAlH(OBu-*t*)$_3$.

1. Introduction

Non-racemic α-amino epoxides are versatile synthetic modules. Nucleophilic ring opening of such epoxides provides a powerful synthetic repertoire for homochiral 1,2-amino alcohols and has found widespread application in the synthesis of natural products, non-peptidic protease inhibitors[1a–c] and chiral auxiliaries.[1e–g] In view of such varied utilities, considerable effort has been directed in recent years towards stereoselective synthesis of non-racemic *threo*- and *erythro*-α-amino epoxides.[2] There are several methods currently available by which *erythro*-α-amino epoxides can be prepared with high diastereoselectivities (≥90% de).[2,3] However, in contrast, the stereoselective synthesis of *threo*-α-amino epoxides (e.g. **1**) is poorly documented and confined to less than a handful of methods that are either lengthy and/or plagued with methodological problems, thus representing a major synthetic hurdle in contemporary asymmetric synthesis. At present, *threo*-α-amino epoxides are best prepared via (i) diastereoselective epoxidation of enantiopure secondary allyl amines (prepared by Wittig reaction of enantiopure α-amino aldehydes),[4a,b] (ii) reactions of enantiopure *N*-Boc α-amino aldehydes with sulfonium/arsonium ylides,[4c,d] and (iii) LAH reduction of chiral pool derived *N*,*N*-dibenzyl α-amino chloromethyl ketones followed by MeLi induced epoxide formation.[4e] While the former two suffer from methodological problems arising from handling the chemically sensitive and racemization-prone

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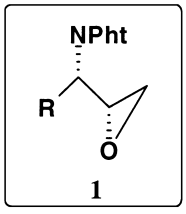
α-amino aldehydes, the latter method which, although avoids the use of α-amino aldehydes, nevertheless requires a non-conventional procedure for the preparation of the starting chloromethyl ketones. In view of these problems, and given the enormous potential of *threo*-α-aminoepoxides in the synthesis of *syn*-1,2-amino alcohols which are common structural units present in a number of anti-HIV dipeptide isosteres and new generation pharmaceutics,[1a–d] it is highly desirable that new and improved procedures be developed for their stereoselective synthesis. To this end, we now describe a facile new synthetic protocol which, while using conventional and chemically stable intermediates, delivers *threo*-*N*-phthaloyl-α-amino epoxides **1** in a short synthetic sequence and with high diastereoselectivity.



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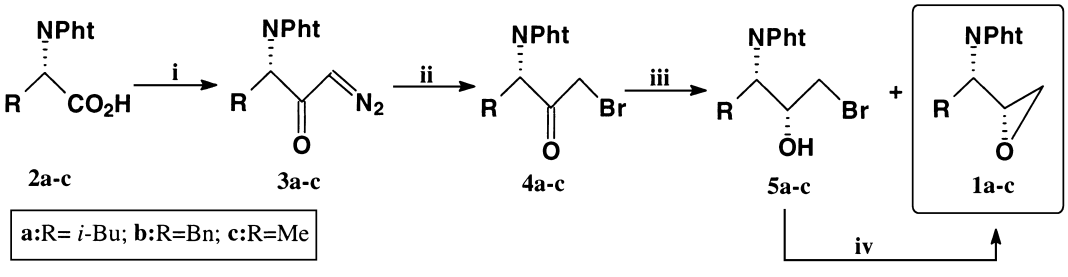
2. Results and discussion

Our synthesis started with the readily available *N*-phthaloyl (*N*-Pht) α-amino acids **2a–c**. The corresponding enantiopure α-amino diazoketones **3a–c** were prepared in good yields (60–70%) by conventional procedures[5,6] and were easily converted via HBr treatment (47% HBr, ether, 0°C) to the corresponding bromoketones **4a–c** in near quantitative yields (Scheme 1, Table 1). The latter were subsequently reduced with LiAlH(OBu-*t*)$_3$ (2 equiv., THF, −20°C) to produce the respective bromohydrins **5a–c** (60–62%) with virtually complete *syn*-selectivity (*syn*:*anti*=95:5). LiAlH(OBu-*t*)$_3$, a bulky and highly chemoselective reducing agent,[7] was found to be absolutely essential for this reduction since other reducing agents viz. NaB(CN)H$_3$ or NaBH$_4$ caused extensive attack on the phthaloyl moiety. Generally, 2 equiv. of LiAlH(OBu-*t*)$_3$ were required for complete reduction of the bromoketones **4a–c**. Small amounts of the *threo*-epoxides **1a–c** were also produced in this reduction step via in situ cyclization of the bromohydrins. Although the bromohydrins could be easily separated from the epoxides and cyclized to the latter, separately with NaH, we found it more convenient to treat this product mixture with NaH in THF at room temperature which smoothly produced the *threo*-α-amino epoxides **1a–c** in good overall yields (62–70%, Table 1), starting from the respective bromoketones.



Scheme 1. (i) $SOCl_2$, benzene, reflux, then CH_2N_2, ether, 0°C; (ii) 47% HBr, ether, 0°C; (iii) LiAlH(OBu-*t*)$_3$ (2 equiv.), THF, −20°C; (iv) NaH, THF, rt

While stereochemical assignments to the bromohydrins were made only after cyclization to the corresponding epoxides (vide infra), none of the other bromohydrin diastereomers (i.e. the *anti*-isomers) were detected in the ^{1}H NMR of the reduction products. The *threo*-stereochemistry of these epoxides was easily deduced from the ^{1}H NMR chemical shifts of the diagnostic epoxide methine protons which,

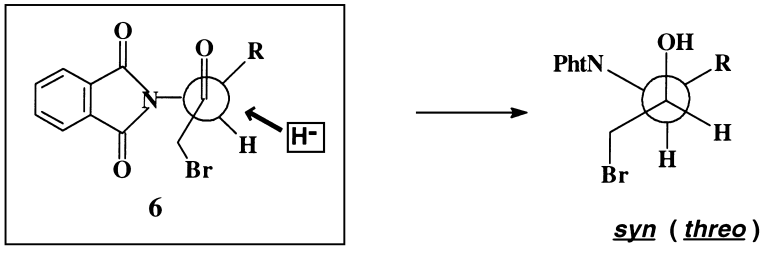
Table 1
Synthesis of α-amino epoxides (Scheme 1)

Entry	R	α-Amino-bromoketones 4	α-Amino-epoxides 1[a]
1	*i*-Bu	4a (84%)	1a (62%)
2	CH_2Ph	4b (88%)	1b (65%)
3	Me	4c (85%)	1c (70%)

[a] overall yields from **4**

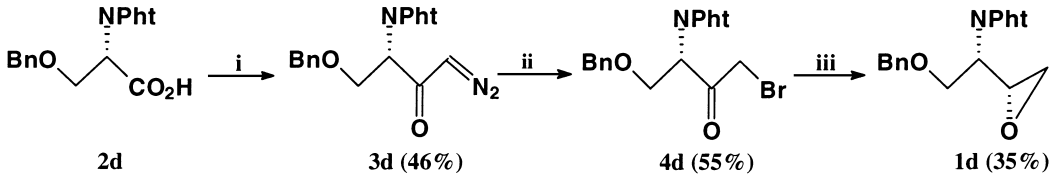
according to the literature,[3b,4b,f] appear at a more downfield position in the *threo*-epoxides than in the *erythro*-isomers. Thus, for example, the oxirane methine proton of **1b** appears at 3.71 ppm, which is ca. 0.2 ppm downfield from the reported value of the same methine proton in the *erythro*-isomer.[8] This, in turn, also confirmed the high degree of *syn*-selectivity in the $LiAlH(OBu\text{-}t)_3$ reduction of the α-amino bromoketones **4**.

The high *syn*-selectivity observed in the bromoketone reductions can be rationalized by a Felkin non-chelation model such as **6**, in which the *N*-Pht moiety acts as a large electronegative group and the bulky reducing agent attacks this TS from the less hindered side.[9] An alternative TS that would have led to the *anti*-bromohydrins is disfavored since it would lead to severe non-bonding and dipolar repulsions between the *N*-Pht and the carbonyl groups. It is worthy of mention that such a high degree of *syn*-selectivity in the reduction of α-amino ketones has otherwise been observed only with the *N*,*N*-dibenzyl systems (Reetz protocol).[10] The present observation that *N*-Pht α-amino ketones, having a more conventional amino protecting group than the *N*,*N*-Bn_2 system, can also be reduced with high *syn*-selectivity, thereby promises a more attractive synthetic protocol for homochiral *syn*-1,2-amino alcohols, in general.



However, *threo*-α-amino epoxides starting from *N*-Pht, *S*-valine and *R*-phenyl glycine could not be prepared by the above method. In these cases, although the α-*N*-Pht diazoketones and the corresponding bromoketones could be prepared without any event, $LiAlH(OBu\text{-}t)_3$ reduction of these bromoketones led to complex product mixtures. The use of higher equivalents of the reducing agent or by carrying out the reduction at lower temperatures (−78°C) did not improve the situation. Nevertheless, the *S*-serine derived *threo*-epoxide **1d** could be prepared by the above method with high diastereoselectivity (Scheme 2). Thus, *N*-Pht *O*-benzyl serine was converted to the diazoketone **3d** as before and the latter upon treatment with 47% HBr gave yield to the somewhat unstable bromoketone **4d**. $LiAlH(OBu\text{-}t)_3$ reduction of **4d** in THF at −78°C then directly produced the epoxide **1d** via in situ cyclization of the bromohydrin. Although yields in this epoxide synthesis are much lower than those obtained for **1a**–**c**, a limitation which is currently being probed for further improvements, diastereoselective synthesis of **1d** by the above methodology is quite significant since this particular epoxide, which is otherwise difficult to synthesize,[11a] is a potentially useful chiron for the synthesis of several biologically active amino polyols and amino sugars.[11b]

In summary, we have described an expeditious new synthesis of non-racemic *threo*-α-amino epoxides.



2d 3d (46%) 4d (55%) 1d (35%)

Scheme 2. (i) $(COCl)_2$, CH_2Cl_2, rt, then CH_2N_2, ether, 0°C; (ii) 47% HBr, ether, 0°C; (iii) $LiAlH(OBu\text{-}t)_3$ (3 equiv.), THF, −78°C

The methodology, by virtue of its high diastereoselectivity and procedural simplicity, should find widespread synthetic applications.

3. Experimental

All melting points are uncorrected. IR spectra were taken on a Perkin–Elmer R-297 spectrometer. ^1H NMR spectra were recorded in $CDCl_3$ (TMS) on JEOL FX-100 (100 MHz), Bruker DPX-200 (200 MHz) and DPX-300 (300 MHz) instruments. Chemical shifts are reported in the ppm scale. Optical rotations were measured in $CHCl_3$ at 25°C on a JASCO DIP-360 polarimeter. The enantiopure *N*-Pht α-amino diazoketones **3a**–**c** were prepared from the corresponding *N*-Pht α-amino acids **2a**–**c** as described in the literature.[5]

*3.1. (S)-4-Benzyloxy-1-diazo-3-phthalimidobutan-2-one **3d***

To a solution of *O*-benzyl-*N*-phthaloyl serine **2d** (0.50 g, 1.53 mmol) in CH_2Cl_2 (5 ml) were added oxalyl chloride (0.29 g, 0.2 ml, 2.28 mmol) and a drop of dry DMF at 0°C. After 45 min, all volatiles were removed under reduced pressure and the crude acid chloride thus obtained was dissolved in CH_2Cl_2 (5 ml) and added dropwise to an ice-cold solution of CH_2N_2 (CAUTION: extreme carcinogen) [prepared from nitrosomethyl urea (1.25 g) and KOH (0.50 g) in water (2 ml) in ether (30 ml)] over 20 min. The reaction was allowed to reach room temperature and excess diazomethane was destroyed with a few drops of HOAc. After addition of satd $NaHCO_3$ solution (10 ml), the ether layer was separated and the aqueous portion extracted with ether (2×10 ml). The combined ether fractions were dried, evaporated under reduced pressure and the residue purified by silica gel chromatography (15% EtOAc in pet. ether) to give **3d** (0.25 g, 46%).

Mp 59–61°C (pet. ether–EtOAc); $[\alpha]_D$ −5.57 (*c* 1.4); IR ($CHCl_3$): 2110, 1710, 1630, 1570 cm^{-1}; ^1H NMR: 4.07 (dd, 1H, *J*=10.1, 7.7 Hz), 4.26 (dd, 1H, *J*=10.1, 6.7 Hz), 4.54 (ABq, 2H, *J*=11.9 Hz), 5.08 (m, 1H), 5.58 (s, 1H), 7.27 (m, 5H), 7.71–7.77 (m, 2H), 7.83–7.88 (m, 2H); found: C, 65.27; H, 4.32; N, 12.01; $C_{19}H_{15}N_3O_4$ requires: C, 65.31; H, 4.29; N, 12.08%.

3.2. General procedure for the preparation of N-*Pht α-amino bromoketones **4a**–**d***

47% HBr (0.20 g, 0.14 ml, 1.2 mmol) was added dropwise to a solution of *N*-Pht α-diazoketones **3a**–**d** (1.0 mmol) in ether (5 ml) at 0°C. After stirring at room temperature for 45 min, the reaction was neutralized with satd $NaHCO_3$ solution and extracted with ether (2×15 ml). The combined ether layer was washed with brine, dried and evaporated under reduced pressure to give the corresponding α-bromoketones **4a**–**d** (Table 1) which were purified either by recrystallization or by silica gel chromatography (pet. ether–EtOAc gradient).

3.2.1. (S)-1-Bromo-5-methyl-3-phthalimidohexan-2-one ***4a***

Oil; $[\alpha]_D$ −3.6 (*c* 1.0); IR (neat): 1770, 1740, 1700 cm^{-1}; ^1H NMR: 0.95 (d, 3H, *J*=6 Hz), 0.98 (d, 3H, *J*=6 Hz), 1.44–1.53 (m, 1H), 1.90–1.99 (m, 1H), 2.17–2.31 (m, 1H), 4.00 (s, 2H), 5.21 (dd, 1H, *J*=3, 12 Hz), 7.76–7.79 (m, 2H), 7.86–7.91 (m, 2H); found: C, 53.02; H, 5.17; N, 4.00; $C_{15}H_{16}BrNO_3$ requires: C, 53.25; H, 4.73; N, 4.14%.

3.2.2. (S)-1-Bromo-4-phenyl-3-phthalimidobutan-2-one ***4b***

Mp 109–110°C (pet. ether–EtOAc); $[\alpha]_D$ −198.8 (*c* 1.0); IR (KBr): 1770, 1700 cm^{-1}; ^1H NMR: 3.38 (dd, 1H, *J*=11, 15 Hz), 3.65 (dd, 1H, *J*=6, 15 Hz), 4.00 (s, 2H), 5.42 (dd, 1H, *J*=6, 11 Hz), 7.16 (s, 5H), 7.68–7.88 (m, 4H); found: C, 58.02; H, 3.74; N, 3.73; $C_{18}H_{14}BrNO_3$ requires: C, 58.08; H, 3.76; N, 3.76%.

3.2.3. (S)-1-Bromo-3-phthalimidobutan-2-one ***4c***

Mp 70–71°C (pet. ether–EtOAc); $[\alpha]_D$ −36.61 (*c* 1.3); IR (KBr): 1780, 1710 cm^{-1}; ^1H NMR: 1.59 (d, 3H, *J*=7.2 Hz), 3.92 (s, 2H), 5.15 (q, 1H, *J*=7.2 Hz), 7.68–7.71 (m, 2H), 7.79–7.83 (m, 2H); found: C, 48.62; H, 3.31; N, 4.7; $C_{12}H_{10}BrNO_3$ requires: C, 48.66; H, 3.37; N, 4.73%.

3.2.4. (S)-4-Benzyloxy-1-bromo-3-phthalimidobutan-2-one ***4d***

Oil; IR ($CHCl_3$): 1770, 1720, 1460 cm^{-1}; ^1H NMR: 3.95 (ABq, 2H, *J*=13 Hz), 3.96 (dd, 1H, *J*=10.4, 8.3 Hz), 4.15 (dd, 1H, *J*=10.4, 5.9 Hz), 4.46 (ABq, 2H, *J*=12 Hz), 5.32 (dd, 1H, *J*=8.3, 5.9 Hz), 7.12–7.18 (m, 5H), 7.68–7.71 (m, 2H), 7.79–7.82 (m, 2H).

*3.3. General procedure for the preparation of threo-*N*-Pht α-amino epoxides* ***1a–c***

$LiAlH(OBu\text{-}t)_3$ (0.51 g, 2.0 mmol) was added portionwise to a solution of the α-*N*-Pht bromoketone **4a–c** (1.0 mmol) in THF (8 ml) at −20°C. After 30 min, the reaction was diluted with ether (25 ml) and washed with water. The organic layer was dried and evaporated under reduced pressure. The residue contained the respective bromohydrins **5a–c** (more polar) together with small amounts of the epoxides **1a–c** (less polar) which were separated by silica gel chromatography (20–25% EtOAc in pet. ether). The bromohydrins **5a–c** (0.5 mmol) were then dissolved in THF (5 ml) and NaH (60% dispersion, 1.5 mmol) was added at 0°C. The mixture was stirred at room temperature until completion of the reaction (3–4 h) after which it was diluted with ether (20 ml) and filtered. The filtrate was washed with water, dried and concentrated under reduced pressure. The residue upon silica gel chromatography (20% EtOAc in pet. ether) then gave the α-amino epoxides **1a–c** which were combined with the less polar fraction obtained previously in the reduction step to calculate the overall yields from the bromoketones (Table 1).

3.3.1. (R)-[(3′-Methyl-1′(S)-phthalimido)butyl]oxirane ***1a***

Oil; $[\alpha]_D$ +13.88 (*c* 1.7); IR (neat): 1770, 1700 cm^{-1}; ^1H NMR: 0.93 (d, 3H, *J*=6 Hz), 0.94 (d, 3H, *J*=6 Hz), 1.48–1.63 (m, 2H), 2.21 (m, 1H), 2.74 (dd, 1H, *J*=3, 5 Hz), 2.92 (dd, 1H, *J*=4.5, 4.5 Hz), 3.60 (ddd, 1H, *J*=3.5, 3.5, 7.4 Hz), 3.99 (ddd, 1H, *J*=4.5, 7.8, 10.5 Hz), 7.73 (m, 2H), 7.85 (m, 2H); found: C, 69.36; H, 6.60; N, 5.32; $C_{15}H_{17}NO_3$ requires: C, 69.49; H, 6.56; N, 5.40%.

3.3.2. (R)-[(2′-Phenyl-1′(S)-phthalimido)ethyl]oxirane ***1b***

Mp 121–122°C (pet. ether–EtOAc); $[\alpha]_D$ −65 (*c* 0.2); IR (KBr): 1780, 1710 cm^{-1}; ^1H NMR: 2.55 (dd, 1H, *J*=2.6, 4.6 Hz), 2.83 (dd, 1H, *J*=4.4, 4.6 Hz), 3.25 (dd, 1H, *J*=7.4, 14 Hz), 3.36 (dd, 1H, *J*=8.8, 14

Hz), 3.71 (ddd, 1H, *J*=2.6, 4.8, 8 Hz), 4.15 (ddd, 1H, *J*=8, 8, 8 Hz), 7.19 (m, 5H), 7.69 (m, 2H), 7.79 (m, 2H); found: C, 73.42; H, 5.23; N, 4.70; $C_{18}H_{15}NO_3$ requires: C, 73.72; H, 5.11; N, 4.77%.

*3.3.3. (*R*)-[1′(*S*)-Phthalimidoethyl]oxirane* ***1c***

Mp 95–96°C (pet. ether–EtOAc); $[\alpha]_D$ +16.16 (*c* 1.2); IR (KBr): 1770, 1710 cm^{-1}; ^1H NMR: 1.50 (d, 3H, *J*=7.2 Hz), 2.73 (dd, 1H, *J*=2.4, 4.8 Hz), 2.9 (dd, 1H, *J*=4.5, 4.5 Hz), 3.60 (ddd, 1H, *J*=2.4, 3.8, 7.7 Hz), 4.06 (qnt, 1H, *J*=7.2 Hz), 7.71 (m, 2H), 7.83 (m, 2H); found: C, 66.00; H, 5.23; N, 6.38; $C_{12}H_{11}NO_3$ requires: C, 66.35; H, 5.06; N, 6.45%.

*3.4. (*R*)-[(2′-Benzyloxy-1′(*S*)-phthalimido)ethyl]oxirane* ***1d***

$LiAlH(OBu\text{-}t)_3$ (0.12 g, 0.47 mmol) was added to a solution of the bromoketone **4d** (0.09 g, 0.22 mmol) in THF (5 ml) at −78°C. After 1 h at this temperature, another portion of $LiAlH(OBu\text{-}t)_3$ (0.06 g, 0.24 mmol) was added to the reaction mixture. After stirring for a further 1 h, water was added at −78°C and the mixture extracted with ether (3×10 ml). The ether layer was dried, concentrated under reduced pressure and the residue chromatographed on silica gel (20% EtOAc in pet. ether) to give the α-amino epoxide **1d** (0.025 g, 35%).

Oil; $[\alpha]_D$ −0.5 (*c* 1.2); IR ($CHCl_3$): 1780, 1710 cm^{-1}; ^1H NMR: 2.74 (m, 1H), 2.90 (m, 1H), 3.62 (m, 1H), 3.88–4.03 (m, 2H), 4.22 (dd, 1H, *J*=14.5, 7.4 Hz), 4.52 (ABq, 2H, *J*=12 Hz), 7.25 (m, 5H), 7.71–7.73 (m, 2H), 7.82–7.85 (m, 2H); found: C, 70.61; H, 5.11; N, 4.21; $C_{19}H_{17}NO_4$ requires: C, 70.59; H, 5.25; N, 4.35%.

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