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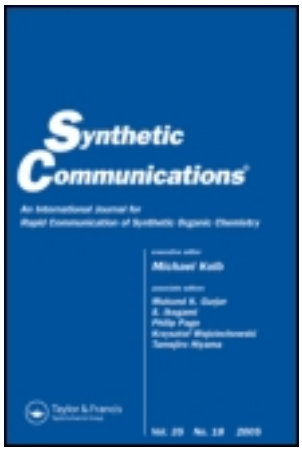

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A Simple and Direct Synthesis of Erythro-β-amino-α-hydroxy Esters from trans-β-Phenylglycidic Ester

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A Simple and Direct Synthesis of Erythro-β-amino-α-hydroxy Esters from *trans*-β-Phenylglycidic Ester

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ABSTRACT

trans-β-Phenylglycidic esters undergo ring opening when treated in *tert*-butyl alcohol with primary amines ($R-NH_2$, with R = secondary group or tertiary group), which attacks epoxide exclusively at C-3 and avoids aminolysis of the ester group affording the erythro-β-amino-α-hydroxy esters as the sole product.

Key Words: Erythro-β-amino-α-hydroxy esters; *tert*-Butyl alcohol; Biological activity; *trans*-β-Phenylglycidic ester; Ester group.

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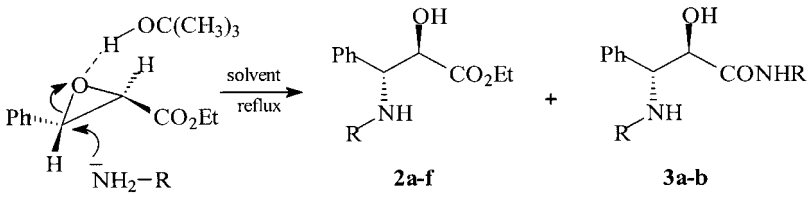
INTRODUCTION

β-Phenylglycidic esters are important intermediates for the synthesis of biologically active compounds.[1–4] Here in, we investigate the reactivity of these epoxides towards nucleophiles. They are known to be attractive building blocks for the synthesis of β-amino-α-hydroxy esters **2**, moiety in the biological activity of compounds that show interesting pharmacological properties such as bestatin, pepstatin,[1] and taxol.[2,3]

The ring opening of β-phenylglycidic esters has been accomplished with a variety of different nucleophilic agents and has been extensively studied.[2,4] However, there are few reports concerning nucleophilic ring opening of these epoxides by amine reagents, which is the frequently used method for the generation of β-amino-α-hydroxy esters. Early work showed that epoxides could be opened with ammonia, benzylamine, and hydrazine, allowing in some cases the obtention of amide[3,5–9] or a mixture[10] of ester and amide. These methods do not effect the ring opening of epoxide without an aminolysis of ester group. However, only two examples which use aromatic amines[5,6,11] or sodium azide[1,12] as nucleophiles, readily gave the ester product. It is worthy to note that early literature[5,6] gives scant information and some results reported on the direction of opening of epoxide are somewhat conflicting.

Here, we report a total regio-, chemo-, and stereoselective synthesis of erythro-β-amino-α-hydroxy esters **2**, in one step, from the reaction of *trans*-β-phenylglycidic ester as starting materials, easily prepared from Darzens reaction,[13] with primary amines ($R-NH_2$, with R = secondary or tertiary group) under refluxing in *tert*-butyl alcohol (Sch. 1). Note that the traditional preparation of **2** requires more than one step.[3,4f,14]

The mechanism of formation maybe understood as one in which the alcohol acted as a weak acid, protonating[15] the epoxide and participate in its opening by the nucleophilic attack of amine exclusively to the C-3 leading to the trans opening product (erythro ester). When reaction is carried out in a non-protic solvent such as toluene or acetonitrile no product was obtained. Moreover, we argue that the steric bulk of the substitutent group of both



Scheme 1.

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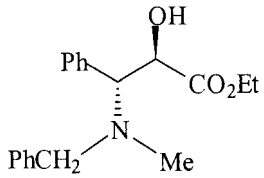
alcohol and amines might improve the chemoselectivity exhibited for this reaction, thus minimizing the amount of unwanted amide compounds **3** to the point that its formation is prevented.

In order to confirm this hypothesis, we have examined more closely the steric effect exerted by both amine and solvent. During the course of this investigation, we noticed that no difference was found when the reaction of β-phenylglycidic ester with benzylamine was achieved in ethanol[10] or *tert*-butyl alcohol and gave predominantly the erythro ester **2a** (entry 1, Table 1). The undesirable amide product **3a** was formed in a low yield. Similarly, the analogous reaction in ethanol with more encumbered amine like isopropylamine furnished the products **2b** and **3b** in modest yields (entry 2, Table 1). Nevertheless, the same reaction carried out in *tert*-butyl alcohol was found to proceed slower and provided the erythro ester **2b** as a single product in good yield. These results suggest that the incursion of the steric effect exerted simultaneously by both amine and solvent is necessary to avoid formation of amide **3**.

To generalize these results, other amines (R = secondary group) were similarly refluxed in *tert*-butyl alcohol with epoxide and the products **2b–e** were isolated in 77–90% yields. As seen in Table 1, the completely regio- and chemoselective C-3 attack of amine, when the substituent at the nitrogen atom was secondary group, occurred in all cases given the desired product **2** in high yields. With more bulky amine (R = tertiary group) (entry 7, Table 1), reaction took a longer time and led to moderate yield (58%) of the desired product.

Single crystals of the ethyl (erythro)-3-phenyl-3-tertbutylamino-2-hydroxypropionate **2f** were analyzed by x-ray crystallography. (Fig. 1).

It should be noted that we have extended the present reaction to secondary amines. Thus, when epoxide was treated with *N*-methylbenzylamine the same reaction was observed and afforded the ethyl 3-phenyl-3-*N*-methylbenzylamino-2-hydroxypropionate **2g** in 94% yield as a single erythro-isomer. This study will be the subject of a future report.



2g

Further conversion and application for the compounds **2**, thus obtained, are now under investigation in our laboratory. They are potentially useful intermediates for the synthesis of β-lactams[16] and aziridines.[10]

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Table 1. Synthesis of erythro-β-amino-α-hydroxy esters **2a–f** and amides **3a–b**.

Entry	R	Solvent	Reaction time (hr)	Ester	Yield (%)	Mp (°C)	Amide	Yield (%)	Mp (°C)
1	$CH_2-C_6H_5$	*t*-Butanol	48	**2a**[a]	76	74	**3a**[a]	19	164
2	*i*-C_3H_7	Ethanol	24	**2b**	43	100	**3b**	26	172
3	*i*-C_3H_7	*t*-Butanol	72	**2b**	84	100	—	—	—
4	$CH(CH_3)C_2H_5$	*t*-Butanol	72	**2c**	77	70	—	—	—
5	$CH(CH_3)C_6H_5$	*t*-Butanol	48	**2d**	90	128	—	—	—
6	C_6H_{11}	*t*-Butanol	48	**2e**	84	102	—	—	—
7	*t*-C_4H_9	*t*-Butanol	120	**2f**	58	94	—	—	—

Note: All reactions were carried out in a large excess of amines (3 eq.). All the yields refer to isolated chromatographically pure compounds.

[a]Mentioned in Refs.[6,8,10].

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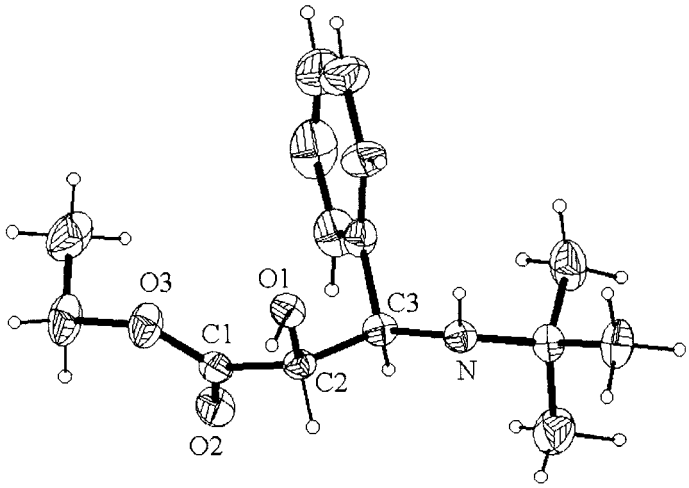

Figure 1. Structure of compound **2f** as determined by x-ray analysis.

In conclusion, we have shown that β-phenylglycidic ester reacts with primary amines to afford a totally chemo-, regio-, and stereoselective reactions with the exclusive formation of the β-amino-α-hydroxy esters by the choice of the substituent at the nitrogen atoms as well as the nature of the solvent.

EXPERIMENTAL

All reagents were purchased from Acros. Reaction progress was monitored by TLC on silica gel plates (Fluka Kieselgel 60 F_{254}). For column chromatography, Fluka Kieselgel 70–230 mesh was used. The infrared (IR) spectra were determined on a Perkin–Elmer Paragon 1000 PC. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AM 300 spectrometer in $CDCl_3$ as solvent and TMS as the internal standard. Mass spectra (GC-MS) were measured on a HP 5890 A mass spectrometer at 70 eV. Microanalyses were performed by the "Service de Microanalyse de l'Institut National de Recherche et d'Analyse Physico-Chimique."

Preparation of Ethyl (Erythro)-3-phenyl-3-alkylamino-2-hydroxypropionate 2b–g: General Procedure

To a solution of β-phenylglycidic ester (5 mmol) in alcohol solvent (10 mL) (*tert*-butyl alcohol for entry 1, 3–7 and ethanol for entry 2), amine

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(15 mmol) was added. The solution was stirred at reflux for the time indicated in Table 1. When the epoxide disappearance was completed (monitored by TLC), the solvent was removed and the residue was purified by flash chromatography using $CHCl_3$/EtOAc (7 : 3) as eluent. Compounds **2b–f** and **3b** were crystallized from hexane.

Ethyl (Erythro)-3-phenyl-3-*i*-propylamino-2-hydroxypropionate (2b). IR ($CHCl_3$, ν, cm^{-1}): 3525, 3331, 1731. ^1H NMR (300 MHz $CDCl_3$): 7.27 (m, 5H), 4.48 (d, 1H, $J = 4.2$ Hz), 4.14 (d, 1H, $J = 4.2$ Hz), 4.03 (q, 2H, $J = 6.9$ Hz), 2.90 (br, 2H, OH and NH), 2.68 (m, 1H), 1.12 (t, 3H, $J = 6.9$ Hz), 1.06 (d, 3H, $J = 6.6$ Hz), 1.02 (d, 3H, $J = 5.8$ Hz). ^{13}C NMR (75 MHz $CDCl_3$): 172.7 (CO_2), 138.1 (C_{arom}), 128.3, 127.8, 127.7 (CH_{arom}) 73.4 (*C*HOH), 61.6 and 61.3 (Ph*C*HN and CH_2O), 45.1 (CH_3CHN), 23.9 and 21.9 ($2CH_3CHN$), 14.0 (CH_3CH_2O). M.S. m/z (%): 252 (MH^+, 0.5%), 178 (4), 148 (100), 106 (51), 91 (17), 79 (12.5). Anal. calcd. for $C_{14}H_{21}NO_3$: C, 66.91; H, 8.42; N, 5.57. Found: C, 66.78; H, 8.50; N, 5.22.

Ethyl (Erythro)-3-phenyl-3-*s*-butylamino-2-hydroxypropionate (2c). IR ($CHCl_3$, ν, cm^{-1}): 3525, 3336, 1731. ^1H NMR (300 MHz $CDCl_3$): 7.25 (m, 5H), 4.50 and 4.48 (2d, 1H, $J = 4.2$ Hz), 4.17 and 4.15 (2d, 1H, $J = 4.2$ Hz), 4.02 (m, 2H) 3.60 (br, 2H, OH and NH), 2.53 and 2.41 (2m, 1H), 1.57–1.29 (m, 2H), 1.12 and 1.11 (2t, 3H, $J = 6.9$ Hz), 1.04 and 0.97 (2d, 3H, $J = 6.2$ Hz), 0.87 and 0.86 (2t, 3H, $J = 7.3$ Hz). ^{13}C NMR (75 MHz $CDCl_3$): 172.5 (CO_2), 138.3, and 137.8, (C_{arom}), 128.2, 127.7, 127.6 (CH_{arom}), 73.5 and 72.9 (*C*HOH), 61.5, 61.3, 61.1, 61.0 (PH*C*HN and CH_2O), 51.0 and 50.7 (CH_3CHN), 30.3 and 28.4 (CH_3CH_2CH), 20.3 and 19.0 (CH_3CHN), 13.9 (CH_3CH_2O), 10.3 and 9.6 (CH_3CH_2CH). M.S. m/z (%): 266 (MH^+, 1%), 236 (2), 192 (3), 162 (100), 106 (70), 91 (29), 79 (15), 77 (9.5). Anal. calcd. for $C_{15}H_{23}NO_3$:C, 67.90; H, 8.74; N, 5.28. Found: C, 67.02; H, 8.67; N, 5.27.

Ethyl (Erythro)-3-phenyl-3-(α-methylbenzyl)amino-2-hydroxypropionate (2d). IR ($CHCl_3$, ν, cm^{-1}): 3520, 3336, 1728. ^1H NMR (300 MHz $CDCl_3$): 7.30 (m, 10H), 4.40 (d, 1H, $J = 4.2$ Hz), 3.97 (m, 2H) 3.76 (d, 1H, $J = 4.2$ Hz), 3.55 (q, 1H, $J = 6.6$ Hz), 3.06 (br, 2H, OH and NH), 1.33 (d, 3H, $J = 6.6$ Hz), 1.05 (t, 3H, $J = 6.9$ Hz). ^{13}C NMR (75 MHz $CDCl_3$): 172.5 (CO_2), 144.5, and 137.8, ($2C_{arom}$), 128.4, 128.3, 128.1, 127.7, 127.0, 126.9 126.6 (CH_{arom}), 73.8 (*C*HOH), 61.6 and 61.2 (Ph*C*HN and CH_2O), 54.6 (CH_3CHN), 25.0 (CH_3CHN), 13.8 (CH_3CH_2O). M.S. m/z (%): 209 (93), 208 (43), 194 (77), 165 (13), 105 (100), 91 (12), 89 (24), 79 (30.5), 77 (68.5). Anal. calcd. for $C_{19}H_{23}NO_3$: C, 72.82; H, 7.40; N, 4.47. Found: C, 72.61; H, 7.32; N, 4.55.

Ethyl (Erythro)-3-phenyl-3-cyclohexylamino-2-hydroxypropionate (2e). IR ($CHCl_3$, ν, cm^{-1}): 3520, 3328, 1728. ^1H NMR (300 MHz $CDCl_3$): 7.28 (m, 5H), 4.51 (d, 1H, $J = 4.2$ Hz), 4.22 (d, 1H, $J = 4.2$ Hz), 4.02 (q, 2H, $J = 6.9$ Hz), 3.10 (br, 2H, OH and NH), 2.36–1.18 (m, 11H), 1.10 (t, 3H, $J = 6.9$ Hz). ^{13}C NMR (75 MHz $CDCl_3$): 172.6 (CO_2), 138.3 (C_{arom}),

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128.3, 128.1, 127.7, 127.6 (CH_{arom}), 73.4 (*C*HOH), 61.1 and 61.0 (Ph*C*HN and CH_2O), 53.2 (CH_2CHN), 34.2, 32.7, 26.0, 24.9, 24.6 (CH_2 cyclohexyl), 14.0 (CH_3CH_2O). M.S. m/z (%): 292 (MH^+, 0.5%), 218 (4), 188 (100), 106 (52), 91 (25), 79 (9.5). Anal. calcd. for $C_{17}H_{25}NO_3$: C, 70.07; H, 8.65; N, 4.81. Found: C, 69.89; H, 8.61; N, 4.82.

Ethyl (Erythro)-3-phenyl-3-*t*-butylamino-2-hydroxypropionate (2f). IR ($CHCl_3$, ν, cm^{-1}): 3524, 3346, 1732. ^{1}H NMR (300 MHz $CDCl_3$): 7.38–7.16 (m, 5H), 4.00 (m, 2H), 3.95 (s, 2H), 3.50 (br s, 1H), 2.50 (s, 1H), 1.13 (t, 3H, $J = 6.9$ Hz), 0.88 (s, 9H). ^{13}C NMR (75 MHz $CDCl_3$): 174.5 (CO_2), 143.9 (C_{arom}), 128.3, 127.8, 127.4, 126.3 (CH_{arom}), 75.6 (*C*HOH), 59.5 and 59.3 (Ph*C*HN and CH_2O), 50.6 (CH_3C), 29.9 ($3CH_3C$), 13.9 (CH_3CH_2O). M.S. m/z (%): 266 (MH^+, 0.5%), 250 (3), 192 (3), 162 (58), 106 (100), 91 (25), 79 (14). Anal. calcd. for $C_{15}H_{23}NO_3$: C, 67.90; H, 8.74; N, 5.28. Found: C, 67.51; H, 8.79; N, 5.27.

Ethyl (Erythro)-3-phenyl-3-*N*-methylbenzylamino-2-hydroxypropionate (2g). IR ($CHCl_3$, ν, cm^{-1}): 3524, 1732. ^{1}H NMR (300 MHz $CDCl_3$): 7.15 (m, 5H), 4.69 (d, 1H, $J = 5.8$ Hz), 4.00 (q, 2H, $J = 6.9$ Hz), 3.73 (d, 1H, $J = 5.8$ Hz), 3.50 and 3.21 (AB, 2H, $J = 13.4$ Hz), 3.03 (s, 1H), 2.10 (s, 3H), 1.05 (t, 3H, $J = 6.9$ Hz). ^{13}C NMR (75 MHz $CDCl_3$): 173.0 (CO_2), 138.9 and 135.8 ($2C_{arom}$), 128.6, 128.5, 128.4, 127.3, 126.9 (CH_{arom}), 71.4 and 70.9 (*C*HOH) and Ph*C*HN), 61.3 and 59.3 (PhCH_2N and CH_2O), 38.7 (CH_3N), 14.1 (CH_3CH_2O). M.S. m/z (%): 240 (2), 210 (90), 118 (7), 91 (100), 77 (4). Anal. calcd. for $C_{19}H_{23}NO_3$: C, 72.82; H, 7.40; N, 4.47. Found: C, 72.64; H, 7.41; N, 4.51.

(Erythro)-3-phenyl-*N*,*N*′-diisopropyl-isoserinamide (3b). IR ($CHCl_3$, ν, cm^{-1}): 3680, 3606, 3409, 1661. ^{1}H NMR (300 MHz $CDCl_3$): 7.28 (m, 5H), 6.63 (d, 1H, $J = 8.4$ Hz), 4.44 (d, 1H, $J = 4.5$ Hz), 4.40 (br s, 1H), 4.22 (d, 1H, $J = 4.5$ Hz), 3.80 (m, 1H), 2.71 (m, 1H), 1.09 (d, 3H, $J = 6.2$ Hz), 1.05 (d, 3H, $J = 6.6$ Hz), 1.01 (d, 3H, $J = 6.6$ Hz), 0.61 (d, 3H, $J = 6.2$ Hz). ^{13}C NMR (75 MHz $CDCl_3$): 170.6 (CO_2), 137.8 (C_{arom}), 128.1, 128.0, 127.6 (CH_{arom}), 72.8 (*C*HOH), 60.8 (Ph*C*HN), 45.4 and 40.2 (*C*HNHCHPh and *C*HNHCO), 23.4, 22.3, 22.1, 21.5 ($4CH_3CHN$). M.S. m/z (%): 147 (29.5), 132 (100), 105 (58), 104 (31.5), 89 (20), 77 (50.5). Anal. calcd. for $C_{15}H_{24}N_2O_2$: C, 68.15; H, 9.15; N, 10.60. Found: C, 67.34; H, 8.94; N, 10.19.

X-Ray Crystallographic Analysis of Compound (2f)

Crystal data: $C_{15}H_{23}NO_3$; monoclinic, space group $P2_1/n$; $a = 14.794(3)$, $b = 6.888(2)$, $c = 15.501(4)$ Å, $\beta = 101.08(2)^\circ$, $V = 1550.1(7)$ Å^3, $Z = 4$, $D_c = 1.14\,g\,cm^{-3}$. Intensity data collected with $\theta \leq 22^\circ$ using Mo Kα radiation (0.71073 Å) on an Enraf-Nonius CAD4 diffractometer; $T = 293$ K, 2199

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reflections measured; 1899 reflections observed [$I \geq 3\sigma(I)$]; solution by direct methods; full matrix least-squares refinement using SHLXL-97 (Sheldrick, G. M. SHELXL-97. Program for the Refinement for Crystal Structures. University of Göttingen, Germany, 1997); non-hydrogens anisotropic, all hydrogen atoms obtained by Fourier-difference and refined isotropically. An ORTEP view of the molecule (johnson, C. K., ORTEPIII, for Windows-Farrugia, L. J. (1997) J. Appl. Cryst. 30, 565) is shown in Fig. 1. The molecules in the crystal are connected by two hydrogen bonds: O1–H2–N [O1–H2 = 0.435(5), H2–N ($1 - x$, $-y$, $1 - z$) = 1.938(1) Å, O1–H2–N = 165.29(1)°] and N-H1–O2 [N–H1 = 0.844 (3), H1–O2 (x, $-1 + y$, z) = 2.488 (1) Å, N–H1–O2 = 162.19(2)°].

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