Abstract — A diastereocconversion of threo 2-amino alcohols to erythro isomers was achieved by treatment of N-Boc derivatives with thionyl chloride or with methanesulfonyl chloride in the presence of triethylamine, hereby cis-4,5-disubstituted oxazolidin-2-ones being produced.

Recently, stereoselective construction of 2-amino alcohols have been greatly stimulated in peptidomimetic chemistry and pharmacological research. Several methods for a stereochemically controlled synthesis of 2-amino alcohols have been reported. Diastereocconversion of one isomer to another would be an important subject from both synthetic and medicinal points of view. Recently, we reported the new facile method for diastereocconversion of 2-amino alcohols without racemization. We further investigated a diastereocversion of N-alkylated threo 2-amino alcohols, obtained through an alkylation of oxazolidin-2-one at the 4-position with high diastereoselectivity. Treatment of N-t-butoxycarbonyl threo 2-amino alcohols with thionyl chloride under the conditions reported previously or with methanesulfonyl chloride in the presence of triethylamine yielded 4,5-cis-oxazolidin-2-ones, which are synthetic equivalent of erythro isomers. The results of our studies are described in this paper. At first threo 2-amino alcohols (7a-e) were prepared according to the method reported previously with high diastereoselectivity as outlined in the Scheme 1. Reduction of the carbamates (3a-c,e), obtained by the reaction of la-c and Za-d, with diisobutylaluminum hydride (DIBAL-H) followed by treatment with ethanol at pH 1-2 afforded the desired 4-ethoxy-5-substituted oxazolidin-2-ones (5a-c, 5e), respectively. 5-Benzyl-4-ethoxyoxazolidin-2-one (5d) was obtained by reduction of 4 with sodium borohydride followed by treatment with ethanol at pH 1-2. The compound (4) was in turn obtained by condensation of methyl a-hydroxyphenylpropionate (1c) and methyl isocyanate (2a). Allylation of 5a-e with allyltrimethylsilane in the presence of titanium tetrachloride gave the corresponding trans-4-allyl-5-substituted oxazolidin-2-ones (6a-e) in 82-88 % yield, as a single diastereomer in all cases. Cleavage of oxazolidinone ring of 6a-e (10 % aq. EtOH-NaOH, reflux, 10 h) gave the corresponding threo 2-amino alcohols (7a-e), respectively in yield shown in the Table 1. t-Butoxycarbonylation
Scheme 1

\[
\begin{align*}
R_1 & \text{COOMe} + R=NR_2 & \rightarrow & & R_1 & \text{COOMe} \\
& \text{OH} & & & 3 & \text{OH} \\
1a: R=Me & & 2a: R=Me & & b: R=\text{CH}_2\text{CHMe}_2 & & c: R=\text{CH}_2\text{C}_6\text{H}_5 \\
b: R=\text{CH}_2\text{CHMe}_2 & & b: R=\text{Et} & & c: R=n-\text{Pr} & & d: R=\text{CH}_2\text{C}_6\text{H}_5 \\
c: R=\text{CH}_2\text{C}_6\text{H}_5 & & c: R=n-\text{Pr} & & & & \\
d: R=\text{CH}_2\text{C}_6\text{H}_5 & & & & & & \\
\end{align*}
\]

\[
\begin{align*}
& \text{R}=\text{Me} \\
& \text{R}=\text{CH}_2\text{CHMe}_2 \\
& \text{R}=\text{CH}_2\text{C}_6\text{H}_5 \\
\end{align*}
\]

For 3-10, 12

\[
\begin{align*}
a: R_1=\text{Me}, R_2=n-\text{Pr} \\
b: R_1=\text{Me}, R_2=\text{CH}_2\text{C}_6\text{H}_5 \\
c: R_1=\text{CH}_2\text{CHMe}_2, R_2=\text{Me} \\
d: R_1=\text{CH}_2\text{C}_6\text{H}_5, R_2=\text{Me} \\
e: R=\text{CH}_2\text{C}_6\text{H}_5, R_2=\text{Et} \\
\end{align*}
\]

\[
\begin{align*}
& \text{SOCl}_2 \\
& \left[\text{Cl}\text{OSO}\right] \\
& \left[\text{R}_1\text{NR}_2\right] \\
& \text{R}_1\text{NR}_2\text{Cl}^{-} \\
9 & \rightarrow & 10(a-d, e) \\
\end{align*}
\]

\[
\begin{align*}
7d & \rightarrow & 10d \\
11a: R=\text{CH}_2\text{C}_6\text{H}_5 \\
b: R=\text{CH}_2\text{CH}=\text{CH}_2 \\
\end{align*}
\]
of 7a-e (Boc$_2$O, Et$_3$N, CH$_2$Cl$_2$, 0°C, 4 h) gave 8a-e, respectively. Treatment of 8a-e with thionyl chloride (0°C → room temperature, 14 h) yielded the corresponding cis-4,5-disubstituted oxazolidin-2-ones (10a-e) with high diastereoselectivity. The relative configuration at 4- and 5-positions of 10a-e was clearly determined by comparison of the chemical shifts and coupling constants for 4-H (δ 3.19, dt, J=5.5, 6 Hz) and 5-H (δ 4.29, dq, J=5.5, 6 Hz) of 6b with those for 4-H (δ 3.61, dt, J=7, 6 Hz) and 5-H (δ 4.81, dq, J=7, 7 Hz) of 10b in their $^1$H-nmr (CDCl$_3$) spectra (see Table 1). The relative configuration of 10a,c,e also determined as 4,5-trans without ambiguity by comparison of chemical shifts for 4-H and 5-H of 6a,c,e with those of 10a,c,e, though their coupling constants are not determined precisely (see Table 1). Apparently this new cyclocarbamation reaction proceeded through S$_N$2 type C-O bond formation as depicted in 9. The same reaction by the use of carbamates (11a,b), derived from 7d, also afforded 10d in 92% yield. Thus, allyl carbamate was also found to be effective for this S$_N$2 type cyclocarbamation as well as N-Cbz$^5$ and N-Boc derivatives. Next, we examined the similar diastereocconversion under non-acidic conditions. Treatment of 8a,d,e with methanesulfonyl chloride in the presence of triethylamine (CH$_2$Cl$_2$, 0°C → room temperature, 14 h) also afforded 10a,d,e in 85, 83 and 80% yield, respectively. Since 4,5-cis-oxazolidin-2-ones are synthetic equivalents of erythro 2-amino alcohols (12a-e), this reaction establishes a new and facile method for diastereocconversion of 2-amino alcohols. The reaction described in this paper would be widely applicable to a diastereocconversion of a variety of 2-amino alcohols and the method would be superior to the other existing methods.$^{3,4,8}$

**Experimental**

All melting points are uncorrected. $^1$H-nmr are determined on a Varian EM-390 instrument with tetramethylsilane as an internal standard. Mass spectra (ms) are determined with a Hitachi RMU-7L instrument. Ir spectra are taken on a Hitachi 260-30 infrared spectrophotometer.

**General Procedure for a Synthesis of Carbamates (3a-c,e)** — A mixture of α-hydroxy ester (1a-c) (50 mmol), isocyanate (2a-d)(55 mmol) and toluene (30 mL) was heated at 100°C for 4 h. The solvent was removed and the residual oil was purified by distillation for 3a,c and 3b,e were purified by column chromatography on silica gel using benzene as an eluant. El ms did not give M$^+$ ion peak but CI ms gave M$^+$ ions. Yields and physical data are as follows.

**Carbamate (3a)** — 95% yield, bp 150-160°C (3 mmHg), ir (CHCl$_3$) 1720, 1750 cm$^{-1}$, $^1$H-nmr (CDCl$_3$) δ 0.93 (3H, t, J=7 Hz), 1.46 (3H, d, J=7 Hz), 1.34-1.74 (2H, m), 3.16 (2H, q, J=7 Hz), 3.74 (3H, s), 5.08 (1H, q, J=7 Hz).

**Carbamate (3b)** — 88% yield, ir (CHCl$_3$) 1720, 1750 cm$^{-1}$, $^1$H-nmr (CDCl$_3$) δ 1.41 (3H, d, J=7 Hz), 3.68 (3H, s), 4.41 (2H, d, J=6 Hz), 5.06 (1H, q, J=7 Hz), 7.27 (5H, broad s).
Carbamate (3c) — 85 % yield, bp 110-115°C (3 mmHg), ir (CHCl₃) 1720, 1740 cm⁻¹, ¹H-nmr (CDCl₃) δ 0.96 (6H, d, J=6 Hz), 1.33 (3H, m), 2.79 (3H, d, J=6 Hz), 3.77 (3H, s), 4.94-5.09 (1H, m).

Carbamate (3e) — 90 % yield, ir (CHCl₃) 1720, 1750 cm⁻¹, ¹H-nmr (CDCl₃) 1.08 (3H, t, J=6 Hz), 1.33 (3H, m), 2.79 (3H, d, J=6 Hz), 3.77 (3H, s), 4.94-5.09 (1H, m).

5-Benzyl-3-methyloxazolidine-2,4-dione (4) — A mixture of methyl α-hydroxyphenylpropionate (1c) (9 g, 50 mmol), methyl isocyante (2a) (8.55 g, 0.15 mmol), and toluene (25 ml) was heated at 100°C for 4 h and then pyridine (20 ml) was added to the reaction mixture and further heated at 145°C for 10 h. The solvent was evaporated and the remaining residue was chromatographed on silica gel (30 g) by using benzene as an eluant. Removal of the solvent gave 4 (8.55 g, 83 % yield) as an oil, CI ms 206 (M⁺+1), ir (CHCl₃) 1740 cm⁻¹, ¹H-nmr (CDCl₃) δ 2.87 (3H, s), 3.07 (1H, dd, J=5.5, 15 Hz), 3.31 (1H, dd, J=4.5, 15 Hz), 4.98 (1H, dd, J=4.5, 5.5 Hz), 7.26 (5H, broad s).

General Procedure for a Synthesis of 4-Ethoxy-5-substituted Oxazolidin-2-ones (5a-e) — For 5a-c,e, to a stirred solution of 3a-c,e (33 mmol) in toluene (50 ml) was added a solution of DIBAL-H (56 ml of 1M hexane solution, 56 mmol) at -78°C. After the stirring had been continued for 40 min at the same temperature, the mixture was decomposed with water. Inorganic precipitate was removed by filtration and the filtrate was extracted with CHCl₃. The extract was dried (Na₂SO₄) and evaporated. To a stirred solution of the remaining residue in EtOH (100 ml) was added conc. HCl (6 ml) at room temperature. After the stirring had been continued for 4 h, the mixture was made basic with sat. NaHCO₃. The solvent was evaporated and the resulting residue was extracted with CHCl₃. Removal of the solvent gave 4-ethoxyoxazolidin-2-ones as a 1:1 mixture of 4.5-cis- and trans-isomer; this was used for the following reaction without purification. For 5d, to a stirred solution of 4 (7 g, 34 mmol) in MeOH (100 ml) was added NaBH₄ (2 g, 61 mmol) in small portions under cooling below 0°C. After the stirring had been continued for 2 h, the solvent was evaporated below 40°C and the resulting residue was diluted with water and extracted with CHCl₃. The solvent was dried (Na₂SO₄) and evaporated. The resulting residue was treated with EtOH as above to yield the 4-ethoxy derivative which was used for the following reaction without purification.

General Procedure for a Synthesis of trans-4-Allyl-5-substituted Oxazolidin-2-ones (6a-e) — To a solution of 5 (20 mmol) in CH₂Cl₂ (20 ml) was added TiCl₄ (7.3 ml of 3 M solution in CH₂Cl₂, 22 mmol) under ice-cooling. After 3 min, allyltrimethylsilane (7.5 g, 30 mmol) was added at the same temperature. After the stirring had been continued for 12 h at room temperature, the mixture was poured onto ice-water and made basic with 28 % ammonia and extracted with CHCl₃. The extract was dried (Na₂SO₄) and evaporated. The resulting residue was chromatographed on silica gel (30 g). Elution with hexane-AcOEt (5:1) gave 6a-e as an oil in all the entries. EI ms did not give M⁺ ion peaks, but CI ms gave M⁺+1 ion. Yields and physical data are given in the Table 1.
Table 1. Yields and Physical Properties of 6a-e, 7a-e, 8a-e and 10a-e

<table>
<thead>
<tr>
<th></th>
<th>Yield</th>
<th>CI m/z</th>
<th>1'H-nmr (CDCl₃) δ</th>
<th>H-nmr (CDCl₃) δ</th>
<th>Physical Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>6a</td>
<td>88 %</td>
<td>184 (M⁺+1)</td>
<td>1730 cm⁻¹</td>
<td>0.89 (3H, t, J=7 Hz)</td>
<td>1.32 (3H, d, J=6 Hz)</td>
</tr>
<tr>
<td>6b</td>
<td>82 %</td>
<td>232 (M⁺+1)</td>
<td>1730 cm⁻¹</td>
<td>1.28 (3H, d, J=6 Hz)</td>
<td>2.22-2.42 (2H, m), 3.19 (1H, dt, J=5.5, 6 Hz, 4-H), 4.10 (1H, d, J=16 Hz)</td>
</tr>
<tr>
<td>6c</td>
<td>87 %</td>
<td>198 (M⁺+1)</td>
<td>1740 cm⁻¹</td>
<td>0.97 (6H, d, J=6 Hz)</td>
<td>1.19-2.03 (3H, m), 2.29-2.53 (2H, m), 2.85 (3H, s), 3.19-3.38 (1H, m, 4-H), 4.10-4.31 (1H, m, 5-H), 5.07-5.34 (2H, m), 5.53-5.99 (1H, m)</td>
</tr>
<tr>
<td>6d</td>
<td>86 %</td>
<td>232 (M⁺+1)</td>
<td>1740 cm⁻¹</td>
<td>2.14-2.30 (2H, m), 2.76 (3H, s)</td>
<td>2.88-2.99 (2H, m), 3.29-3.47 (1H, m, 4-H), 4.26-4.46 (1H, m, 5-H), 4.94-5.17 (2H, m), 5.56-6.13 (1H, m), 7.27 (5H, broad s)</td>
</tr>
<tr>
<td>6e</td>
<td>85 %</td>
<td>246 (M⁺+1)</td>
<td>1740 cm⁻¹</td>
<td>0.96 (3H, t, J=7 Hz)</td>
<td>2.17-2.31 (2H, m), 2.73-3.13 (3H, m), 3.27-3.67 (1H, m), 3.41-3.60 (1H, m, 5-H), 4.31-4.50 (1H, m, 5-H), 4.97-5.23 (2H, m), 5.40-5.83 (1H, m), 7.31 (5H, broad s)</td>
</tr>
<tr>
<td>7a</td>
<td>85 %</td>
<td>182 (M⁺+1)</td>
<td>1740 cm⁻¹</td>
<td>0.93 (3H, t, J=7 Hz)</td>
<td>1.17 (3H, d, J=6 Hz), 1.26-1.62 (2H, m), 2.12-2.49 (2H, m), 2.33-2.51 (3H, m), 3.88-4.14 (1H, m), 5.03-5.26 (2H, m), 5.60-6.06 (1H, m)</td>
</tr>
<tr>
<td>7b</td>
<td>97 %</td>
<td>206 (M⁺+1)</td>
<td>1740 cm⁻¹</td>
<td>1.20 (3H, d, J=6 Hz)</td>
<td>2.09-2.59 (3H, m), 3.33-3.59 (1H, m), 3.67 (1H, d, J=12 Hz), 3.89 (1H, d, J=12 Hz), 5.57-6.02 (1H, m), 7.31 (5H, broad s)</td>
</tr>
<tr>
<td>7c</td>
<td>87 %</td>
<td>172 (M⁺+1)</td>
<td>1740 cm⁻¹</td>
<td>0.90 (3H, d, J=6 Hz)</td>
<td>0.94 (3H, d, J=6 Hz), 1.21-1.40 (2H, m), 1.48-2.43 (3H, m), 3.23-3.50 (2H, m), 4.93-5.20 (2H, m), 5.52-5.98 (1H, m)</td>
</tr>
<tr>
<td>7d</td>
<td>96 %</td>
<td>206 (M⁺+1)</td>
<td>1740 cm⁻¹</td>
<td>2.17-2.53 (2H, m)</td>
<td>2.41 (3H, s), 2.67-2.87 (2H, m), 3.50-3.70 (1H, m), 4.94-5.23 (2H, m), 5.56-6.03 (1H, m), 7.26 (5H, broad s)</td>
</tr>
<tr>
<td>7e</td>
<td>96 %</td>
<td>220 (M⁺+1)</td>
<td>1740 cm⁻¹</td>
<td>1.08 (3H, t, J=7 Hz)</td>
<td>2.10-3.03 (5H, m), 3.49-3.70 (1H, m), 5.02-5.18 (2H, m), 5.59-6.06 (1H, m), 7.28 (5H, broad s)</td>
</tr>
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continue
continued

8a  92% yield, $^1$H-nmr (CDCl$_3$) $\delta$ 0.87 (3H, t, $J$=7 Hz), 1.19 (3H, d, $J$=6 Hz), 1.46 (9H, s), 1.28-1.78 (2H, m), 2.41-2.64 (2H, m), 2.99-3.34 (3H, m), 3.71-4.00 (1H, m), 5.00-5.19 (2H, m), 5.60-6.06 (1H, m).

8b  90% yield, $^1$H-nmr (CDCl$_3$) $\delta$ 1.04 (3H, d, $J$=6 Hz), 1.50 (9H, s), 2.33-2.54 (2H, m), 3.20-3.63 (1H, m), 3.63-3.97 (1H, m), 4.37 (2H, s), 4.88-5.10 (2H, m), 4.90-5.31 (1H, m), 7.30 (SH, broad s).

8c  93% yield, $^1$H-nmr (CDCl$_3$) $\delta$ 0.90 (3H, d, $J$=6 Hz), 0.96 (3H, d, $J$=6 Hz), 1.19-1.39 (2H, m), 1.46 (9H, s), 1.53-1.94 (1H, m), 2.26-2.49 (2H, m), 2.67-2.83 (1H, m), 2.78 (3H, s), 3.49-3.79 (1H, m), 4.92-5.19 (2H, m), 5.49-6.00 (1H,

8d  92% yield, $^1$H-nmr (CDCl$_3$) $\delta$ 1.43 (9H, s), 2.28-2.58 (2H, m), 2.64-2.94 (1H, m), 2.79 (3H, s), 3.68-3.98 (1H, m), 4.92-5.20 (2H, m), 5.53-5.98 (1H, m), 7.27 (SH, broad s).

8e  90% yield, $^1$H-nmr (CDCl$_3$) $\delta$ 1.14 (3H, t, $J$=7 Hz), 1.48 (9H, s), 2.39-2.84 (2H,m), 3.04-3.62 (3H, m), 3.76-4.03 (1H, m), 4.97-5.19 (2H, m), 5.58-6.03 (1H, m), 7.24 (5H, broad s).

10a 90% yield, CI ms m/z 184 (M$^+$+1), ir (CHCl$_3$) 1730 cm$^{-1}$, $^1$H-nmr (CDCl$_3$) $\delta$ 0.92 (3H, t, $J$=7 Hz), 1.37 (3H, d, $J$=6 Hz), 1.18-1.70 (2H, m), 2.26-2.49 (2H, m), 2.84-3.16 (1H, m), 3.28-3.61 (1H, m), 3.70-3.97 (1H, m, 4-H), 4.50-4.80 (1H, m, 5-H), 4.62-4.96 (2H, m), 5.57-6.02 (1H, m).

10b 85% yield, CI ms m/z 232 (M$^+$+1), ir (CHCl$_3$) 1730 cm$^{-1}$, $^1$H-nmr (CDCl$_3$) $\delta$ 1.36 (3H, d, $J$=6 Hz), 2.24-2.41 (2H, m), 3.61 (1H, dt, $J$=7, 6 Hz, 4-H), 4.08 (1H, d, $J$= 16 Hz), 4.60 (1H, dq, $J$=7, 7 Hz, 5-H), 4.81 (1H, d, $J$=16 Hz), 4.98-5.23 (2H, m), 5.40-5.91 (1H, m), 7.30 (5H, broad s).

10c 90% yield, CI ms m/z 198 (M$^+$+1), ir (CHCl$_3$) 1740 cm$^{-1}$, $^1$H-nmr (CDCl$_3$) $\delta$ 0.93 (3H, d, $J$=6 Hz), 0.97 (3H, d, $J$=6 Hz), 1.19-2.01 (3H, m), 2.26-2.50 (2H, m), 2.83 (3H, s), 3.59-3.81 (1H, m, 4-H), 4.44-4.68 (1H, m, 5-H), 5.02-5.30 (2H, m), 5.57-6.02 (1H, m).

10d 92% yield, CI ms m/z 232 (M$^+$+1), ir (CHCl$_3$) 1740 cm$^{-1}$, $^1$H-nmr (CDCl$_3$) $\delta$ 2.40-2.57 (2H, m), 2.87 (3H, s), 2.98-3.07 (2H, m), 3.67-3.88 (1H, m, 4-H), 4.61-4.84 (1H, m, 5-H), 5.12-5.33 (2H, m), 5.64-6.10 (1H, m), 7.29 (5H, broad s).

10e 90% yield, CI ms m/z 246 (M$^+$+1), ir (CHCl$_3$) 1740 cm$^{-1}$, $^1$H-nmr (CDCl$_3$) $\delta$ 1.17 (3H, t, $J$=7 Hz), 2.41-2.54 (2H, m), 2.97-3.30 (3H, m), 3.39-3.78 (1H, m), 3.79-3.98 (1H, m, 4-H), 4.58-4.81 (1H, m, 5-H), 5.09-5.31 (2H, m), 5.63-6.08 (1H, m), 7.28 (5H, broad s).
General Procedure for a Synthesis of threo 2-Amino Alcohols (7a-e) — A mixture of 6a-e (10 mmol), EtOH (27 ml) and 50 % NaOH (6 g) was heated under reflux for 10 h. After removal of the solvent, the remaining residue was diluted with water and extracted with CHCl₃. The extract was dried (Na₂SO₄) and evaporated. The residual oil was chromatographed on silica gel by using CHCl₃ as an eluant. Removal of the solvent gave 7a-e as an oil. Yields and physical properties of 7a-e are listed in Table 1.

General Procedure for t-Butyloxycarbonylation of 7a-e — To a mixture of 7 (7 mmol), Et₃N (1.41 g, 14 mmol), and CH₂Cl₂ (5 ml) was added di-t-butyl dicarbonate (1.31 g, 7 mmol) under ice-cooling. After 2 h, the mixture was decomposed with water and extracted with CHCl₃. The extract was washed with water, dried (Na₂SO₄) and evaporated. The resulting residue was chromatographed on silica gel (15 g). Elution with hexane afforded uncharacterized product which was discarded. Successive elution with hexane-AcOEt (7:1) gave 8a-e as an oil in all entry. ¹H-nmr spectral data of which were listed in the Table 1.

Benzyl Carbamate (11a) — To a stirred mixture of 7d (1 g, 4.88 mmol), Et₃N (1.0 g, 9.9 mmol), CH₂Cl₂ (5 ml) was added benzyl chloroformate (3.5 ml of 30 % toluene solution) under ice-cooling. After the stirring had been continued for 40 min at the same temperature, the mixture was poured onto ice-water and extracted with CHCl₃. The mixture was washed with 5 % HCl, water, dried (Na₂SO₄) and evaporated. The remaining oil was chromatographed on silica gel (10 g) by using hexane-AcOEt (9:1) as an eluant. Removal of the solvent gave 11a as an oil (1.46 g, 88 % yield). ¹H-nmr (CDCl₃) δ 2.27-3.00 (5H, m), 2.89 (3H, s), 3.70-4.00 (1H, m), 4.96-5.33 (2H, m), 5.15 (2H, s), 5.51-6.00 (1H, m), 7.25 (5H, broad s), 7.36 (5H, broad s).

Allyl Carbamate (11b) — To a stirred mixture of 7d (1 g, 4.88 mmol), Et₃N (1.0 g, 9.9 mmol), CH₂Cl₂ (5 ml) was added a solution of allyl chloroformate (0.62 g, 5.12 mmol) in CH₂Cl₂ (5 ml) under ice-cooling. After the stirring had been continued at the same temperature for 1 h, the mixture was poured onto water and extracted with CHCl₃. The extract was washed with 5 % HCl, water, dried (Na₂SO₄) and evaporated. The remaining residue was chromatographed on silica gel (10 g) by using hexane-AcOEt (9:1) as an eluant. Removal of the solvent gave 11b (1.20 g, 85 % yield). ¹H-nmr (CDCl₃) δ 2.31-2.58 (2H, m), 2.61-3.18 (3H, m), 2.88 (3H, s), 3.70-4.01 (1H, m), 4.52-4.66 (2H, m), 4.94-5.41 (4H, m), 5.53-6.16 (2H, m), 7.26 (5H, broad s).

General Procedure for the Reaction of 8a-e with Thionyl Chloride — To a solution of 8a-e (2.53 mmol) in CH₂Cl₂ (5 ml) was added SOCl₂ (3 g, 25.3 mmol) under ice-cooling. After the stirring had been continued for 10 h at room temperature, the mixture was poured onto ice-water and made basic with 28 % ammonia. The mixture was extracted with CHCl₃. The extract was washed with water, dried (Na₂SO₄) and concentrated. The remaining residue was chromatographed on silica gel (15 g) by using...
Removal of the solvent gave 1Da-e. These compounds were obtained as an oil except 10d: mp 81-82°C. Anal. Calcd for C_{14}H_{18}NO_{2}: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.46; H, 7.35; N, 6.04. Yields and physical data were listed in the Table 1.

General Procedure for the Reaction of 1la,b with Thionyl Chloride — To a stirred solution of 1la (or 1lb) (2.5 mmol) in CH$_2$Cl$_2$ (5 ml) was added SOCl$_2$ (3 g, 25.3 mmol) under ice-cooling. After the stirring had been continued for 10 h at room temperature, the mixture was worked up as above to give 10d (450 mg (78% yield) from 1la and 530 mg (92% yield) from 1lb).

General Procedure for the Reaction of 8a,d,e with Methanesulfonyl Chloride-Triethylamine — To a stirred solution of 8a,d,e (5 mmol), Et$_3$N (1.01 g, 10 mmol), CH$_2$Cl$_2$ (5 ml) was added a solution of CH$_3$SO$_2$Cl (0.63 g, 5.5 mmol) in CH$_2$Cl$_2$ (5 ml) under ice-cooling. After the stirring had been continued for 14 h, the mixture was poured onto water and extracted with CHC$_3$. The extract was washed with 5% HCl, dried (Na$_2$SO$_4$) and evaporated. The remaining residue was chromatographed on silica gel (10 g) by using hexane-AcOEt (5:1) as an eluant. Removal of the solvent gave 10a (0.76 g, 83% yield), 10d (0.96 g, 83% yield), 10e (0.98 g, 80% yield), respectively, which were identical with those of authentic samples obtained from 8a,d,e.

REFERENCES


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