A NOVEL SYNTHESIS OF CHIRAL DBU/DBN-RELATED MOLECULES FOR USE IN ASYMMETRIC BASE CATALYSIS

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Abstract --- The synthesis of sterically hindered chiral DBU/DBN-related molecules (6) from (+)-camphor lactam (1) is described. The value of the products as chiral organic base catalysts is exemplified by their use in asymmetric Michael addition reactions of β-keto ester (7).

1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) have attracted considerable interest due to their importance as non-nucleophilic strong organic bases (e.g., pKₐ values in acetonitrile of 23.79 and 24.31 for DBU and DBN respectively) in promoting several types of organic transformation, such as isomerization, esterification, alkylation, Michael addition, condensation, and protection. Accordingly, it is easy to imagine that the introduction of a chiral center onto the DBU/DBN skeleton could provide an efficient entry to novel enantiopure organic base catalysts. Unfortunately, however, very few examples of the synthesis of chiral DBU/DBN derivatives have been reported so far. In our studies toward this end, we were particularly interested in the conformationally rigid structure of (+)-camphor, since there are numerous examples of the successful use of this chiral framework in asymmetric transformation.

In this paper, we describe a novel synthesis of sterically hindered DBU/DBN-related organic bases. Our synthetic strategy toward the target molecule (A) is shown in Scheme 1. To construct an amidine functionality as a crucial step we planned to use the intramolecular condensation of ω-amino-N-alkylated thiolactam B, which can be prepared from (+)-camphor lactam (1), readily available from (+)-camphoric acid, by straightforward manipulation.

Scheme 1
Based on this idea, we proceeded with the synthesis of DBU/DBN-related molecules (6) (Scheme 2). The reaction of 1 with o-azidoalkyl methanesulfonates (2) in the presence of KH in THF gave the o-azido-bearing N-alkylated compounds (3) in good yields. Reductive transformation of the terminal azido group to the corresponding N-(tert-butoxycarbonyl)-protected amines (4) under catalytic hydrogenation conditions, followed by treatment with Lawesson’s reagent in toluene at 100 °C, gave thiolactams (5). Finally, treatment of 5 with excess MeI, followed by deprotection of a Boc group with trifluoroacetic acid in CH2Cl2 at 0 °C, afforded the corresponding ammonium salt which, upon exposure to excess 10% aq NaOH, cyclized smoothly to give the desired amidines (6a) (44% from 4a) and (6b) (47% from 4b), respectively: [α]D24 +24.8° (c = 0.73, MeOH) for 6a and [α]D26 +98.7° (c = 0.40, MeOH) for 6b.

\[
\begin{align*}
1 & \quad + \quad \text{MsO} \quad \overset{a}{\to} \quad 2a: n = 1 \\
& \quad \quad 2b: n = 2 \\
& \quad + \quad \text{N}_{3} \\
& \quad \overset{b}{\to} \quad 3a: n = 1 (82\%) \\
& \quad \quad 3b: n = 2 (68\%) \\
\text{N}_{3} & \quad \overset{c}{\to} \quad 4a: n = 1 (97\%) \\
& \quad \quad 4b: n = 2 (91\%) \\
& \quad \quad \text{N}_{3} \quad \overset{c}{\to} \quad 5a: n = 1 \\
& \quad \quad \quad \text{N}_{3} \quad \overset{c}{\to} \quad 5b: n = 2 \\
& \quad \quad \quad \overset{d}{\to} \quad 6a: n = 1 (44\%) \\
& \quad \quad \quad \quad \quad \overset{d}{\to} \quad 6b: n = 2 (47\%)
\end{align*}
\]

Scheme 2

Reagents and Conditions: (a) KH, THF, 0 °C → rt; (b) H2, 20% Pd(OH)2 / C, (Boc)2O, AcOEt, rt; (c) Lawesson's reagent, toluene, 100 °C; (d) (i) MeI, rt, (ii) CF3COOH, CH2Cl2, 0 °C, (iii) 10% aq NaOH.

To evaluate the chemical and stereochemical behavior of 6 for asymmetric catalysis, we examined the well-studied asymmetric Michael addition reactions of β-keto ester (7) with methyl vinyl ketone (8) in the presence of a catalytic amount of optically active 6a or 6b. The results are summarized in Table 1. In the presence of 10 mol% of 6a, β-keto ester (7) reacted quite smoothly with 8 in EtOH as a solvent at room temperature to give the adduct (9), but with no enantioselectivity (Entry 1). Switching from EtOH solvent to CH2Cl2 did not affect ee (Entry 2). However, the use of a less polar solvent such as CCl4 and toluene appeared to be favorable in terms of enantioselectivity: 9 was obtained in a quantitative yield and with 8 and 7% ee, respectively, in favor of its R-isomer (Entries 3 and 4). The reaction at 0 °C gave no significant increase in enantioselectivity (Entry 5). Quite similar results were obtained for 6b, albeit with less catalytic activity (Entries 7 and 8, 5 and 6% ee, respectively).
Table 1. Asymmetric Michael addition reactions of β-keto ester (7) with MVK (8)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conditions</th>
<th>Yield (%)</th>
<th>ee (%)</th>
<th>Abs. Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6a</td>
<td>EtOH, rt, 1.5 h</td>
<td>100</td>
<td>0</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>6a</td>
<td>CH₂Cl₂, rt, 19 h</td>
<td>97</td>
<td>0</td>
<td>--</td>
</tr>
<tr>
<td>3</td>
<td>6a</td>
<td>CCl₄, rt, 11 h</td>
<td>100</td>
<td>8</td>
<td>R</td>
</tr>
<tr>
<td>4</td>
<td>6a</td>
<td>toluene, rt, 2 h</td>
<td>100</td>
<td>7</td>
<td>R</td>
</tr>
<tr>
<td>5</td>
<td>6a</td>
<td>toluene, 0 °C, 2.5 h</td>
<td>100</td>
<td>8</td>
<td>R</td>
</tr>
<tr>
<td>6</td>
<td>6a</td>
<td>no solvent, rt, 1.5 h</td>
<td>100</td>
<td>0</td>
<td>--</td>
</tr>
<tr>
<td>7</td>
<td>6b</td>
<td>toluene, rt, 19 h</td>
<td>100</td>
<td>5</td>
<td>R</td>
</tr>
<tr>
<td>8</td>
<td>6b</td>
<td>toluene, 0 °C, 70 h</td>
<td>93</td>
<td>6</td>
<td>R</td>
</tr>
</tbody>
</table>

a) Isolated yields. b) Determined by HPLC (DAICEL Chiralpak AD). c) Determined by optical rotation: [α]²⁰⁰° ~77° (c = 2, benzene) for enantiomerically pure (S)-9. See ref. 8.

This unexpectedly disappointing result may be ascribed to the severe steric shielding of both the upper and lower sides of the amidine base face in 6 by a bulky bornane skeleton. The pronounced solvent effect of EtOH undoubtedly indicates its great tendency to solvate the transient intermediates, making the interaction between the reactants and our chiral base catalysts much less severe.

In conclusion, the synthesis of a family of new sterically hindered DBU/DBN-related chiral derivatives (6) was accomplished in a four-step sequence starting from (+)-camphor lactam (1) as a convenient chiral source. Unfortunately, all of these compounds are still unsatisfactory for achieving a high level of asymmetric induction in Michael addition reactions. Further studies on modification of the ligand design and its application to asymmetric synthesis are now underway.

**EXPERIMENTAL**

All melting points are uncorrected. ¹H and ¹³C NMR spectra were recorded on a JEOL LA-400 (400 MHz for ¹H NMR and 100 MHz for ¹³C NMR analysis) spectrometer. All NMR spectra were taken in CDCl₃ solutions and are reported in parts per million (δ) downfield from TMS as an internal standard. The FT-IR spectra (cm⁻¹) were measured with a JASCO Model FT/IR-5300 Fourier transform infrared spectrophotometer. Optical rotations were measured on a JASCO DIP-370 polarimeter. HPLC analyses were carried out using a Hitachi L-6200 HPLC system. Elemental analyses (C, H, N) were performed on
a Perkin Elmer-2400 elemental analyzer. TLC was performed using Merck precoated Kieselgel 60F-254 plates (0.25 mm). Preparative TLC was carried out on 2 mm-thick Merck Kieselgel 60PF-254. Column chromatography was done on Wakogel C-300 (silica gel) or Merck activated neutral alumina 90 (alumina).

3-Azido-1-propyl Methanesulfonate (2a).

1,3-Propanediol mono-THP ether\(^1\) (5 g, 31.2 mmol) was converted into the corresponding mesylate (6.93 g, 93\%) by the usual method. A solution of this mesylate and NaN\(_3\) (2.27 g, 35 mmol) in dry DMF (45 mL) was stirred at 70 °C overnight. After conventional work-up, the crude product was purified by silica gel column chromatography (hexane / AcOEt = 4 : 1) to give the corresponding THP-azido (5.22 g, 97\%) as a pale yellow oil. Deprotection of a THP group (MeOH, Amberlyst H-15, 45 °C, 3 h) followed by mesylation gave 2a (1.54 g, 98\%) as a pale yellow oil: FTIR (neat) \(\nu\) 2101, 1352, 1173; 1H NMR (CDCl\(_3\)) \(\delta\) 2.01 (2H, quintet, \(J = 6.1\) Hz), 3.04 (3H, s), 3.49 (2H, t, \(J = 6.1\) Hz), 4.33 (2H, t, \(J = 6.1\) Hz); 13C NMR (CDCl\(_3\)) \(\delta\) 28.7, 37.3, 47.3, 66.5.

\(\beta\)

(1S,4\(R\))-3-(3-Azidopropyl)-3-aza-4,7,7-trimethylbicyclo[2.2.1]heptan-2-one (3a).

To a suspension of KH (35% suspension in oil; 1.35 g, 13.2 mmol) in THF (100 mL) at 0 °C was added dropwise a solution of (+)-camphor lactam (1) (1.69 g, 11.0 mmol) in THF (50 mL), and the mixture was stirred under Ar for 1 h at rt. A solution of 3-azidopropyl mesylate (2a) (1.97 g, 11.0 mmol) in THF (50 mL) was then added dropwise at 0 °C, and the mixture was stirred for 24 h at rt. After quenching by adding water, the mixture was concentrated \(\text{in vacuo}\) and extracted with AcOEt. The extracts were washed with water and brine, dried (Na\(_2\)SO\(_4\)), and concentrated. The crude product was purified by silica gel column chromatography (hexane / acetone = 4 : 1) to give 3a (2.12 g, 82\%) as a light yellow oil: \(R_f\) 0.40 (hexane / acetone = 2 : 1); \([\alpha]_D^{26\ +}\) +32.2\(^{\circ}\) (c = 0.78, CHCl\(_3\)); FTIR (neat) \(\nu\) 2097, 1698; 1H NMR (CDCl\(_3\)) \(\delta\) 0.89, 0.96, 1.21 (each 3H, s), 1.50 (2H, m), 1.74-1.84 (3H, m), 1.93-2.00 (1H, m), 2.30 (1H, d, \(J = 4.1\) Hz), 3.08 (1H, dt, \(J = 14.1, 7.1\) Hz), 3.26 (1H, dt, \(J = 14.1, 7.1\) Hz), 3.34 (2H, m); 13C NMR (CDCl\(_3\)) \(\delta\) 12.2, 18.1, 18.5, 23.5, 29.3, 33.6, 36.1, 49.3, 49.7, 55.0, 70.7, 178.6; MS \(m/z\) (rel. intensity) 237 (M\(^+\) + 1, 100), 208 (32), 194 (59), 180 (31), 166 (23), 153 (13), 109 (36), 56 (16). HRMS calcd for C\(_{12}\)H\(_{20}\)N\(_4\)O + H, 237.1715, found 237.1694.

In a similar manner, 3b (1.56 g, 68\%) was prepared from 1 (1.40 g, 9.14 mmol) and 2b (1.77 g, 9.16 mmol) as a light yellow oil: \(R_f\) 0.35 (hexane / acetone = 2 : 1); \([\alpha]_D^{23\ +}\) +30.5\(^{\circ}\) (c = 0.98, CHCl\(_3\)); FTIR (neat) \(\nu\) 2097, 1696; 1H NMR (CDCl\(_3\)) \(\delta\) 0.88 (3H, s), 0.96 (3H, s), 1.21 (each 3H, s), 1.44-1.66 (6H, m), 1.79 (1H, dt, \(J = 12.2, 3.9\) Hz), 1.95 (1H, m), 2.29 (1H, d, \(J = 4.1\) Hz), 3.07 (1H, dt, \(J = 14.0, 6.8\) Hz), 3.19 (1H, dt, \(J = 14.0, 6.8\) Hz), 3.32 (2H, t, \(J = 6.3\) Hz); 13C NMR (CDCl\(_3\)) \(\delta\) 12.2, 18.1, 18.5,
23.5, 26.4, 27.1, 33.7, 38.0, 49.8, 51.0, 55.0, 70.6, 178.4; MS m/z (rel. intensity) 251 (M+ + 1, 100), 222 (22), 208 (42), 194 (40), 179 (20), 166 (14), 154 (13), 109 (22), 70 (49). HRMS calcd for C13H22N4O + H, 251.1872, found 251.1867.

(1S,4R)-3-(3-(N-tert-Butoxycarbonyl)aminopropyl)-3-aza-4,7,7-trimethylbicyclo-[2.2.1]heptan-2-one (4a).

A mixture of azidolactam (3a) (680 mg, 2.9 mmol), Boc2O (1.14 g, 5.2 mmol), and a catalytic amount of 20% Pd(OH)2/C in AcOEt (10 mL) was stirred under H2 for 36 h at rt. The inorganic catalyst was removed by filtration through Celite, and the filtrate was concentrated in vacuo. The crude product was purified by silica gel column chromatography (AcOEt) to give 4a (870 mg, 97%) as a colorless oil: Rf 0.47 (AcOEt); [α]D26 +5.1° (c = 0.98, CHCl3); FTIR (neat) ν 3349, 1711, 1688; 1H NMR (CDCl3) δ 0.89, 0.96, 1.19 (each 3H, s), 1.43 (9H, s), 1.40-1.60 (3H, m), 1.60-1.70 (1H, m), 1.74-1.83 (1H, m), 1.94-2.02 (1H, m), 2.31 (1H, d, J = 4.1 Hz), 3.02-3.22 (3H, m), 3.25 (1H, ddd, J = 14.6, 8.8, 5.9 Hz), 5.75 (1H, br); 13C NMR (CDCl3) δ 12.1, 18.1, 18.5, 23.6, 26.8, 28.4 (× 3), 29.9, 33.6, 35.6, 37.2, 50.0, 55.0, 70.8, 78.7, 156.2, 179.4; MS m/z (rel. intensity) 311 (M+ + 1, 27), 255 (36), 237 (39), 211 (100), 194 (15), 167 (19), 83 (12). Anal. Calcd for C17H30N2O3: C, 65.77; H, 9.74; N, 9.02. Found: C, 65.59; H, 9.97; N, 8.94.

In a similar manner, 4b (240 mg, 91%) was prepared from 3b (200 mg, 0.8 mmol) and Boc2O (320 mg 1.4 mmol) as a colorless oil: Rf 0.28 (AcOEt); [α]D23 +21.5° (c = 0.98, CHCl3); FTIR (neat) ν 3339, 1686; 1H NMR (CDCl3) δ 0.87, 0.95, 1.19 (each 3H, s), 1.44 (9H, s), 1.40-1.60 (6H, m), 1.77 (1H, dt, J = 12.2, 3.9 Hz), 1.95 (1H, m), 2.28 (1H, d, J = 4.1 Hz), 3.05-3.20 (4H, m), 4.66 (1H, br); 13C NMR (CDCl3) δ 12.1, 18.1, 18.5, 23.5, 27.2, 27.6, 28.4 (× 3), 33.7, 38.3, 40.1, 49.8, 55.0, 70.6, 79.0, 156.0, 178.3; MS m/z (rel. intensity) 324 (M+, 3), 251 (7), 220 (18), 205 (11), 192 (37), 177 (71), 166 (11), 138 (16), 110 (19), 70 (19), 56 (100). Anal. Calcd for C18H32N2O3: C, 66.63; H, 9.94; N, 8.63. Found: C, 66.51; H, 10.16; N, 8.73.

(1S,4R)-3-(3-(N-tert-Butoxycarbonyl)aminopropyl)-3-aza-4,7,7-trimethylbicyclo-[2.2.1]heptane-2-thione (5a).

A solution of N-Boc-lactam (4a) (100 mg 0.3 mmol) and Lawesson’s reagent (78 mg, 0.2 mmol) in dry toluene (2 mL) was stirred at 100 °C for 3 h under N2. The mixture was concentrated in vacuo to give a brownish oil which was purified by preparative TLC (hexane / AcOEt = 1 : 1) to give thiolactam (5a) (70 mg, 67%) as a white solid: Rf 0.22 (hexane / AcOEt = 2 : 1); FTIR (KBr) ν 3314, 1680, 1513; 1H NMR (CDCl3) δ 0.89, 0.91, 1.29 (each 3H, s), 1.44 (9H, s), 1.40-1.58 (4H, m), 1.76 (2H, t, J = 6.8, 6.1 Hz), 1.86 (1H, ddd, J = 12.9, 9.5, 3.4 Hz), 1.98-2.05 (1H, m), 2.89 (1H, d, J = 4.1 Hz), 3.14 (2H, q, J = 6.1 Hz), 3.68 (2H, t, J = 6.8 Hz), 5.54 (1H, br); 13C NMR (CDCl3) δ 12.2, 18.1, 18.6, 25.2, 28.4 (× 3), 28.7, 34.0, 37.5, 40.9, 52.5, 66.0, 76.5, 79.0, 156.0, 205.8. Anal. Calcd for C17H30N2O2S: C, 62.54; H, 9.26; N, 8.58. Found: C, 62.41; H, 9.29; N, 8.53. This sample was used immediately for the next reaction.
In a similar manner, 5b (160 mg, 74%) was prepared from 4b (205 mg, 0.63 mmol) and Lawesson’s reagent (170 mg, 0.42 mmol) as a white solid: Rf 0.25 (hexane / AcOEt = 2 : 1); FTIR (KBr) ν 3291, 1681, 1476; 1H NMR (CDCl3) δ 0.88, 0.90, 1.29 (each 3H, s), 1.44 (9H, s), 1.40-1.62 (4H, m), 1.69 (2H, br), 1.85 (1H, ddd, J = 12.9, 9.3, 3.7 Hz), 2.00 (1H, ddd, J = 16.6, 9.8, 3.9 Hz), 2.86 (1H, d, J = 4.1 Hz), 3.18 (2H, br d, J = 6.1 Hz), 3.52-3.67 (2H, m), 4.74 (1H, br); 13C NMR (CDCl3) δ 12.2, 18.1, 18.5, 24.8, 25.1, 27.5, 28.4 (x 3), 34.0, 39.7, 43.1, 52.4, 65.9, 76.3, 79.1, 156.0, 204.6. Anal. Calcd for C_{18}H_{32}N_{2}O_{2}S: C, 63.49; H, 9.47; N, 8.23. Found: C, 63.46; H, 9.63; N, 8.11.

(1R,8S)-2,6-Diaza-1,11,11-trimethyltricyclo[6.2.1.0<2,7>]undec-6-ene (6a).

A solution of thiolactam (5a) (181 mg, 0.55 mmol) in MeI (1 mL, 16 mmol) was stirred under N2 for 15 h at rt in the dark. After concentration in vacuo, the crude product was dissolved in dry CH2Cl2 (4 mL), and trifluoroacetic acid (0.4 mL, 5.2 mmol) at 0 °C was added. After stirring at 0 °C for 4 h, the mixture was quenched by adding ice and 10% NaOH. The aqueous layer was extracted with CH2Cl2, and the combined extracts were washed with brine, dried (K2CO3), and concentrated. The residue was purified by alumina column chromatography (AcOEt / MeOH = 9 : 1) to give chiral amide (6a) (42 mg, 44% from 4a) as a pale yellow solid: mp ~30 °C; [α]_D^{22} +24.8° (c = 0.73, MeOH); FTIR (KBr) ν 1672, 1574, 1318; 1H NMR (CDCl3) δ 0.94, 0.97, 1.26 (each 3H, s), 1.58 (2H, m), 1.84-1.95 (2H, m), 2.04-2.14 (1H, m), 2.16-2.25 (1H, m), 3.28 (2H, t, J = 6.0 Hz), 3.44 (1H, ddd, J = 13.9, 7.1, 4.4 Hz), 3.47 (1H, d, J = 3.9 Hz), 3.53 (1H, ddd, J = 13.9, 6.8, 4.9 Hz); 13C NMR (CDCl3) δ 10.7, 17.9, 18.0, 19.4, 24.8, 32.5, 37.1, 38.0, 51.5, 52.2, 74.4, 168.2; MS m/z (rel. intensity) 193 (M+ + 1, 100), 177 (18), 164 (10), 149 (37). HRMS calcd for C_{12}H_{20}N_{2} + H, 193.1706, found 193.1685.

In a similar manner, 6b (270 mg, 47% from 4b) was prepared from 5b (870 mg, 2.55 mmol) as a pale yellow oil: [α]_D^{22} +98.7° (c = 0.40, MeOH); FTIR (neat) ν 1670; 1H NMR (CDCl3) δ 0.95 (6H, s), 1.26 (3H, s), 1.56-1.89 (4H, m), 1.96-2.11 (2H, m), 2.15-2.22 (1H, m), 3.09 (1H, ddd, J = 13.2, 10.2, 2.9 Hz), 3.35-3.46 (2H, m), 3.54 (1H, d, J = 3.9 Hz), 3.75 (1H, ddd, J = 14.4, 5.9, 3.2 Hz); 13C NMR (CDCl3) δ 12.1, 17.8, 18.1, 24.6, 26.5, 26.7, 31.7, 44.1, 45.7, 51.1, 53.5, 76.9, 173.0; MS m/z (rel. intensity) 207 (M+ + 1, 100), 191 (48), 178 (7), 163 (17), 143 (6). HRMS calcd for C_{13}H_{22}N_{2} + H, 207.1861, found 207.1849.

Typical Procedure for the Asymmetric Michael Addition Reaction of β-Keto Ester (7) with Methyl Vinyl Ketone (8).

To a solution of β-keto ester (7) (40 mg, 0.20 mmol) and chiral amide (6a) (4 mg, 0.021 mmol) in dry toluene (0.4 mL) at rt was added methyl vinyl ketone (8) (44 mg, 0.60 mmol), and the mixture was stirred under Ar for 2 h at rt. After concentration in vacuo, the crude product was purified by preparative TLC (hexane / AcOEt = 2 : 1) to yield the adduct (9) (55 mg, 100 %) as a white solid. The enantiomeric excess (ee) of this product was determined by HPLC analysis (254 nm, flow rate: 0.5 mL/min) carried out with Chiralpak AD (eluent: hexane / 2-propanol = 90 : 10, t_R 21.9 min for the S-isomer and t_R 24.3 min for the R-isomer): Rf 0.19 (hexane / AcOEt = 2 : 1); [α]_D^{22} +4.18° (c = 0.96, C_{6}H_{6}) (7% ee by HPLC analysis);
FTIR (KBr) 1734, 1713, 1607; $^1$H NMR (CDCl$_3$) δ 2.13 (3H, s), 2.24 (2H, m), 2.48-2.68 (2H, m), 3.05 (1H, d, $J = 17.3$ Hz), 3.67 (1H, d, $J = 17.3$ Hz), 3.70 (3H, s), 7.42 (1H, t, $J = 7.6$ Hz), 7.48 (1H, d, $J = 7.6$ Hz), 7.64 (1H, t, $J = 7.6$ Hz), 7.78 (1H, d, $J = 7.6$ Hz); $^{13}$C NMR (CDCl$_3$) δ 28.6, 29.9, 37.9, 38.8, 52.7, 59.1, 124.9, 126.4, 128.0, 135.0, 135.5, 152.5, 171.6, 202.3, 207.5.

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REFERENCES AND NOTES
9. 6a showed a similar reactivity compared with DBU itself: in the presence of 10 mol% of DBU the same reaction was completed within 2 h at rt, and 9 was obtained in an almost quantitative yield.