JOC The Journal of Organic Chemistry

J. Org. Chem., 1997, 62(17), 5680-5681, DOI:10.1021/jo971050y

Diastereoselective Enosilane Coupling Reactions Supporting Information

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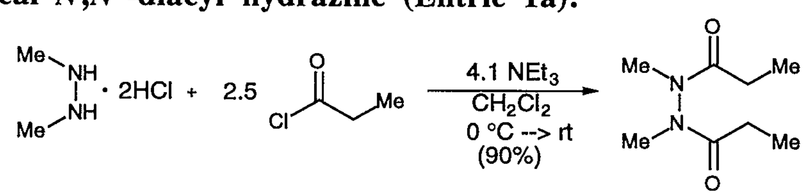
General Procedures.

Proton NMR spectra were recorded on Varian Gemini 400 spectrometer. Proton chemical shifts are reported in ppm (δ) relative to internal tetramethylsilane (TMS, δ 0.0) or with the solvent reference relative to TMS employed as the internal standard ($CDCl_3$, δ 7.26 ppm; DMSO-d_6, δ 2.50). Data are reported as follows: chemical shift (multiplicity [singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m)], coupling constants [Hz], integration). Carbon NMR spectra were recorded on Varian Gemini 400 (100Mhz) spectrometers with complete proton decoupling. Carbon chemical shifts are reported in ppm (δ) relative to TMS with the respective solvent resonance as the internal standard ($CDCl_3$, δ 77.0; DMSO-d_6, δ 39.5). For the *N,N'*-diacyl hydrazines, NMR data are reported for the major rotamer (>90%) observed in solution at ambient temperature. For the *N*-methyl succininimide derivatives, data are reported for the major *trans*-diastereomer, unless otherwise indicated. Infrared spectra were obtained on a Nicolet 210 spectrophotometer. Diagnostic bands are reported (ν_{max} in cm^{-1}). Analytical thin-layer chromatography (TLC) was performed using Silica Gel 60 F254 precoated plates (0.25 mm thickness). TLC R_f values are reported. Visualization was accomplished by irradiation with a UV lamp and/or staining with $KMnO_4$ or Cerium ammonium nitrate (CAM) solutions. Flash column chromatography was performed using Silica Gel 60A (170-400 mesh) from Fisher Scientific.[1] Elemental analyses were performed by Robertson Microlit (Madison, NJ). High resolution mass spectra were obtained at the Mass Spectrometry Facility of the University of Illinois (Urbana-Champaign, IL).

All reactions were carried out under an argon atmosphere employing oven- and flame-dried glassware. All solvents were distilled from appropriate drying agents prior to use. Et_3N was distilled from CaH_2 prior to use. DMSO was dried over 3Å molecular sieves. Trimethylsilyl(trifluoromethanesulfonate) was purchased from the Aldrich Chemical Company, distilled prior to use and stored under Argon.

General Procedures for the Preparation of *N,N'*-Diacyl-*N,N'*-dialkyl hydrazines

Method 1. Symmetrical *N,N'*-diacyl hydrazine (Entrie 1a):

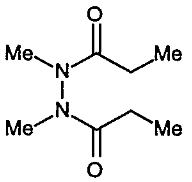


To a 0 °C suspension of *N,N'*-dimethylhydrazine dihydrochloride (0.50 g, 3.76 mmol) in anhydrous methylene chloride was added triethylamine (2.15 mL, 15.4 mmol). After stirring for 20 min, the acid chloride (0.82 mL, 9.44 mmol) was added with vigorous stirring. The reaction was then warmed to rt and was stirred for an

[1] Still, W.C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

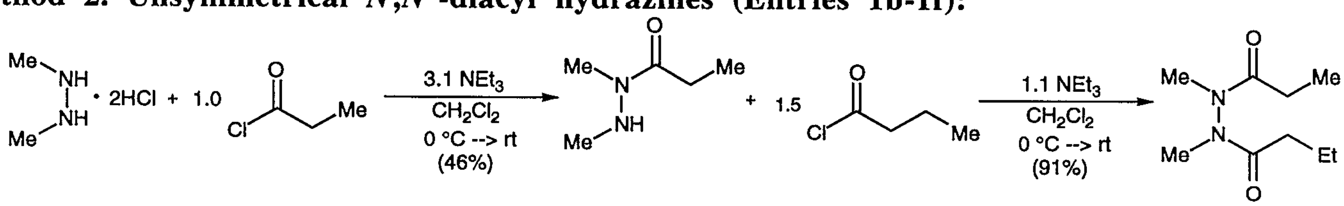
additional 2 h. The reaction mixture was then diluted with 20 mL of methylene chloride, washed with 1N hydrochloric acid (3x15 mL) and was dried over anhydrous sodium sulfate. Evaporation *in vacuo* yielded the crude residue which was purified via flash chromatography chromatography (50% ethyl acetate/hexane) to yield a clear liquid (0.58 g, 89.6%). (R_f 0.29 in 60% ethyl acetate/hexane - stained w/ CAM)

Substrate 1a: (91%)



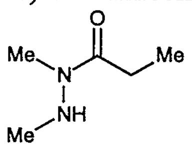
^1H NMR ($CDCl_3$, 400 MHz) δ 3.14 (s, 6H), 2.27 (m, 4H), 1.14 (t, J=7.6 Hz, 6H);
^{13}C NMR ($CDCl_3$, 100 MHz) δ 175.4, 33,3, 24.8, 8.7;
IR (neat, cm^{-1}) 2983, 2942, 1673, 1466, 1423, 1376;
TLC R_f 0.30 (80% ethyl acetate/hexane);
Anal. Calcd. for $C_8H_{16}N_2O_2$: C, 55.79; H, 9.36. Found: C, 55.73; H, 9.02;
Exact mass calcd for $C_8H_{16}N_2O_2$ (M^+) requires *m/z* 172.1212. Found 172.1212 (EI).

Method 2. Unsymmetrical *N,N'*-diacyl hydrazines (Entries 1b-1f):



To a 0 °C suspension of *N,N'*-dimethylhydrazine dihydrochloride (5.50 g, 41.4 mmol in anhydrous methylene chloride was added triethylamine (17.9 mL, 128.4 mmol). After stirring for 20 min, propionyl chloride (3.60 mL, 41.44 mmol) was added dropwise over a 90 min period. The reaction was then allowed to warm to rt and was stirred for an additional 2 hrs. The solvent was then evaporated *in vacuo* and the residue was washed with benzene. The filtrate was evaporated to yield a crude residue which was vacuum fractionally distilled to yield a clear liquid (2.214 g, 46 %). (B.P. 119 °C @ 28 mmHg)
N,N'-dimethyl-*N*-propanoylhydrazine (0.220 g, 1.90 mmol) was combined with 15 mL of anhydrous methylene chloride under Ar. The stirring mixture was then chilled to 0 °C, and to it was added triethylamine (0.29 mL, 2.08 mmol), followed by bromoacetyl bromide (0.30 mL, 2.88 mmol). The reaction was then allowed to warm to rt and was stirred at this temp for 2 hr. After this period the mixture was combined with 20 mL of methylene chloride and was washed with 1N hydrochloric acid (2x15 mL) and the organic layer was dried over anhydrous sodium sulfate. Evaporation *in vacuo* yielded the crude residue which was purified via flash silica chromatography (60% ethyl acetate/hexane) to yield a clear liquid (0.321 g, 91%). (R_f 0.18 in 60% ethyl acetate/hexane - stained w/ CAM)

***N,N'*-dimethyl-*N*-propanoylhydrazine.** (46%)



(1.3:1 - rotamers)

^{1}H NMR rotamer 1 ($CDCl_3$, 400 MHz) δ 3.46 (broad d, J=5.6 Hz, 1H), 3.10 (s, 3H), 2.62 (d, J=5.6 Hz, 3H), 2.54 (q, J=7.6 Hz, 2H), 1.10 (t, J=7.6 Hz, 3H);

^{1}H NMR rotamer 2 ($CDCl_3$, 400 MHz) δ 5.53 (broad s, 3.14 (s, 3H), 2.55 (s, 3H), 2.33 (q, J=7.6 Hz, 2H), 1.163 (t, J=7.6 Hz, 3H);

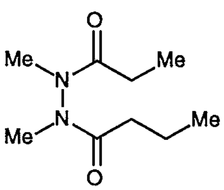
^{13}C NMR both rotamers ($CDCl_3$, 100 MHz) δ 176.4, 171.5, 35.9, 35.4, 35.3, 31.5, 26.0, 25.6, 9.3, 8.9;

IR (neat, cm^{-1}) 3473, 3285, 2981, 2940, 2882, 1640, 1464, 1414, 1386;

Anal. Calcd. for $C_5H_{12}N_2O$: C, 51.70; H, 10.41, N, 24.12. Found: C, 51.63; H, 10.38, N, 23.91;

Exact mass calcd for $C_5H_{12}N_2O$ (M^+) requires *m/z* 116.0950. Found 116.0949 (EI).

Substrate 1b: (91%)



^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.11 (s, 3H), 3.10 (s, 3H), 2.25 (t, J=7.0 Hz, 2H), 2.19 (m, 2H), 1.65 (tq, J=7.6, 7.6 Hz, 2H), 1.13 (t, J=7.6 Hz, 3H), 0.927 (t, 7.6 Hz, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 175.6, 174.8, 33.6, 33.4, 33.3, 24.9, 17.9, 13.8, 8.8;

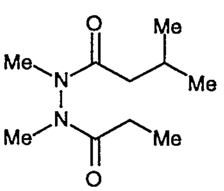
IR (neat, cm^{-1}) 2964, 2936, 2874, 1676, 1461, 1421, 1378;

TLC R_f 0.18 (60% ethyl acetate/hexane);

Anal. Calcd. for $C_9H_{18}N_2O_2$: C, 58.04; H, 9.74, N, 15.04. Found: C, 57.73; H, 9.63, N, 14.80;

Exact mass calcd for $C_9H_{18}N_2O_2$ (M^+) requires *m/z* 186.1368. Found 186.1371 (EI).

Substrate 1c: (81%)



^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.09 (s, 6H), 2.21 (m, 3H), 2.08 (m, 2H), 1.12 (t, J=7.4 Hz, 3H), 0.91 (d, J=6.4 Hz, 3H), 0.90 (d, J=6.4 Hz, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 175.7, 174.4, 40.3, 33.8, 33.4, 24.9, 24.8, 22.7, 22.6, 8.9;

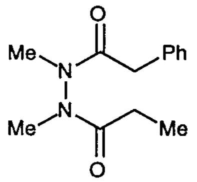
IR (neat, cm^{-1}) 2959, 2872, 1679, 1468, 1417, 1378;

TLC R_f0.18 (40% ethyl acetate/hexane);

Anal. Calcd. for $C_{10}H_{20}N_2O_2$: C, 59.97; H, 10.06, N, 13.99. Found: C, 59.89; H, 10.01, N, 13.77;

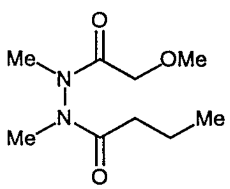
Exact mass calcd for $C_{10}H_{20}N_2O_2$ (M^+) requires *m/z* 200.1525. Found 200.1514 (EI).

Substrate 1d: (68%)



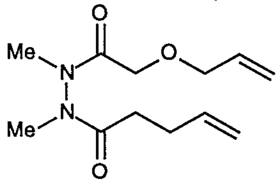
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.23-7.34 (m, 5H), 3.63 (m, 2H), 3.11 (s, 3H), 3.08 (s, 3H), 2.09 (dq, J=7.6, 16.8 Hz, 1H), 1.95 (dq, J=7.6, 16.8 Hz, 1H), 0.98 (t, J=7.6 Hz, 3H);
^{13}C NMR ($CDCl_3$, 100 MHz) δ 176.1, 173.0, 133.5, 129.1, 128.7, 127.2, 39.6, 34.0, 33.7, 25.0, 8.6;
IR (neat, cm^{-1}) 2979, 2932, 1671, 1454, 1415, 1374;
TLC R_f 0.21 (60% ethyl acetate/hexane);
Anal. Calcd. for $C_{13}H_{18}N_2O_2$: C, 66.64; H, 7.74, N, 11.96. Found: C, 66.32; H, 7.61, N, 11.56;
Exact mass calcd for $C_{13}H_{18}N_2O_2$ (M^+) requires *m/z* 234.1368. Found 234.1368 (EI).

Substrate 1e: (66%)



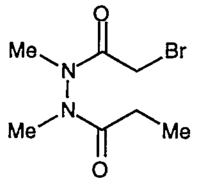
^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.06 (d, J=15.2 Hz, 1H), 4.00 (d, J=15.2 Hz, 1H), 3.45 (s, 3H), 3.14 (s, 3H), 3.13 (s, 3H), 2.24 (m, 2H), 1.68 (apparant q, J=7.2 Hz, 2H), 0.95 (t, J=7.2 Hz, 3H);
^{13}C NMR ($CDCl_3$, 100 MHz) δ 174.9, 170.7, 69.7, 59.4, 33.4, 33.3, 33.2, 17.8, 13.7;
IR (neat, cm^{-1}) 2964, 2931, 1682, 1460, 1421, 1384, 1133;
TLC R_f 0.14 (80% ethyl acetate/hexane);
Anal. Calcd. for $C_9H_{18}N_2O_3$: C, 53.45; H, 8.97, N, 13.85. Found: C, 53.35; H, 8.87, N, 13.77;
Exact mass calcd for $C_9H_{18}N_2O_3$ (M^+) requires *m/z* 202.1317. Found 202.1317 (EI).

Substrate 1f: (96%)



^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.90 (m, 1H), 5.80 (m, 1H), 5.29 (d, J=18 Hz, 1H), 5.24 (d, J=10 Hz, 1H), 5.07 (d, J=18 Hz, 1H), 5.02 (d, J=10 Hz, 1H), 4.09 (m, 4H), 3.14 (s, 3H), 3.12 (s, 3H), 2.4 (m, 4H);
^{13}C NMR ($CDCl_3$, 100 MHz) δ 174.4, 171.0, 136.7, 133.7, 118.5, 116.0, 72.5, 67.0, 33.7, 33.6, 31.0, 28.5;
IR (neat, cm^{-1}) 3080, 2981, 2921, 1680, 1420, 1384, 1331;
TLC R_f 0.23 (60% ethyl acetate/hexane);
Anal. Calcd. for $C_9H_{18}N_2O_3$: C, 59.98; H, 8.39, N, 11.66. Found: C, 59.62; H, 8.34, N, 11.62;
Exact mass calcd for $C_{12}H_{20}N_2O_3$ (M^+) requires *m/z* 241.1552. Found 241.1554 (EI).

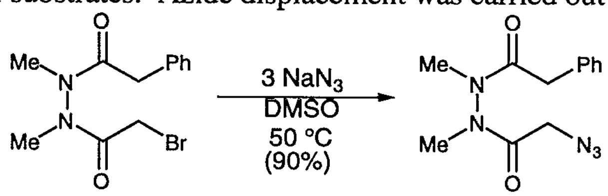
***N*-bromoacetyl-*N,N'*-dimethyl-*N'*-propanoyl hydrazine.** (92%)



^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.89 (m, 2H), 3.21 (s, 3H), 3.18 (s, 3H), 2.43 (q, J=7.6 Hz, 1H), 2.26 (q, J=7.6 Hz, 1H), 1.16 (t, J=7.6 Hz, 3H)
^{13}C NMR ($CDCl_3$, 100 MHz) δ 176.0, 168.6, 128.3, 34.1, 25.2, 24.1, 8.7;
IR (neat, cm^{-1}) 2980, 2941, 1676, 1463, 1421, 1376;
TLC R*f* 0.18 (60% ethyl acetate/hexane);
Anal. Calcd. for $C_7H_{13}BrN_2O_2$: C, 35.46; H, 5.53, N, 11.82. Found: C, 35.15, H, 5.50, N, 11.68;
Exact mass calcd for $C_7H_{13}BrN_2O_2$ (M^+) requires *m/z* 236.0160. Found 236.0159 (EI).

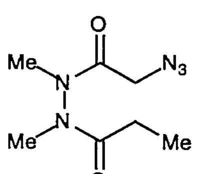
Method 3. Azidoacetyl hydrazides (Entries 1g and 1h):

The *N,N'*-dimethyl-*N*-acyl-*N'*-bromoacetyl hydrazides were prepared according to the general protocol for the preparation of the unsymmetrical substrates. Azide displacement was carried out as follows:



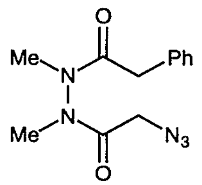
Sodium Azide (1.22 g, 18.8 mmol) was dissolved into 50 mL of anhydrous dimethyl sulfoxide at 50 °C under Ar. *N,N'*-Dimethyl-*N*-bromoacetyl-*N'*-phenylacetylhydrazide (1.87 g, 6.27 mmol) was then added to this solution, and the reaction was stirred at 50 °C under Ar for 24 hrs. The mixture was diluted with 400 mL of distilled water, and the product was extracted into ethyl acetate (5x100 mL). The combined organic layers were washed with water (5x100 mL), brine (1x100 mL) and dried over anhydrous sodium sulfate. Removal of the solvent *in vacuo* afforded a residue which was purified via flash silica chromatography.

Substrate 1g: (54%)



^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.87 (m, 2H), 3.17 (s, 3H), 3.14 (s, 3H), 2.29 (m, 2H), 1.15 (t, J=7.2 Hz, 3H);
^{13}C NMR ($CDCl_3$, 100 MHz) δ 175.5, 169.3, 49.4, 33.6, 33.5, 25.0, 8.7;
IR (neat, cm^{-1}) 2988, 2944, 2110, 1685, 1421, 1377, 1275;
TLC R*f* 0.18 (50% ethyl acetate/hexane);
Anal. Calcd. for $C_7H_{13}N_5O_2$: C, 42.20; H, 6.58, N, 35.16. Found: C, 42.17; H, 6.51, N, 35.19;
Exact mass calcd for $C_7H_{14}N_5O_2$ (M^+) requires *m/z* 200.1148. Found 200.1154 (CI).

Substrate 1h: (90%)



^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.23-7.37 (m, 5H), 3.69 (d, J=14 Hz, 1H), 3.59 (d, J=14, 1H), 3.43 (d, J=16.4 Hz, 1H), 3.15 (s, 3H), 3.09 (s, 3H), 3.07 (d, J=16.4 Hz, 1H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.1. 169.9, 133.1, 129.0, 128.8, 127.6, 49.4, 40.3, 34.1, 34.0;

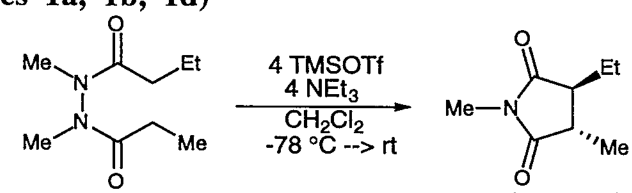
IR (neat, cm^{-1}) 2988, 2944, 2110, 1685, 1421, 1377, 1275;

TLC R_f 0.18 (50% ethyl acetate/hexane);

Anal. Calcd. for $C_{12}H_{15}N_5O_2$: C, 55.16; H, 5.79, N, 26.80. Found: C, 55.52; H, 5.78, N, 26.41;

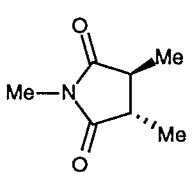
Exact mass calcd for $C_{12}H_{15}N_5O_2$ (M^+) requires *m/z* 261.1226. Found 261.1228 (EI).

General Procedures for the Rearrangement of *N,N'*-diacyl-*N,N'*-dialkyl hydrazines: Method 1. (Table 1, Entries 1a, 1b, 1d)



N,N'-dimethyl-*N*-butanoyl-*N'*-propanoylhydrazide (0.715 g, 3.84 mmol) was dissolved into 35 mL of anhydrous methylene chloride under Ar. The stirring solution was then chilled to -78 °C and to it was added trimethylsilyltrifluoromethanesulfonate (2.78 mL, 15.4 mmol). After stirring the mixture for 5 min, triethylamine (2.14 mL, 15.4 mmol) was added and the solution was stirred for an additional 30 min at -78 °C. After this period the reaction was allowed to warm to rt, and was stirred at this temp for 36 hours. The solution was then evaporated *in vacuo* and purified directly via flash silica chromatography (20% ethyl acetate/hexane) to yield a clear liquid (0.55 g, 93 %). (R_f 0.14 in 20% ethyl acetate/hexane - stained w/$KMnO_4$). (Note: For this substrate, when the reaction temperature is held at -30° C, the observed diastereoselectivity is 7:1).

Product 2a: (66%)



^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.98 (s, 3H), 2.41 (q, J=7.2 Hz, 2H), 1.34 (d, J=7.2 Hz, 6H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 179.6, 43.1, 24.8, 15.0;

IR (neat, cm^{-1}) 2974, 2936, 2880, 1772 (shoulder), 1703, 1438, 1388, 1281;

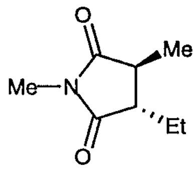
TLC R_f 0.18 (15% ethyl acetate/hexane);

Anal. Calcd. for $C_7H_{11}N_1O_2$: C, 59.56; H, 7.85. Found: C, 59.18; H, 8.00;

Exact mass calcd for $C_7H_{11}N_1O_2$ (M^+) requires *m/z* 141.0790. Found 141.0789 (EI).

Assignment of Stereochemistry for **2a**: Compared directly to samples prepared from meso- and (+/-)-2,3-dimethyl- succinic acid according to the method of Rinehart, *et.al.*[2]

Product 2b: (93%)



^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.98 (s, 3H), 2.51 (dq, J=7.2, 5.0 Hz, 1H), 2.33 (m, 1H), 1.94 (m, 1H), 1.63 (m, 1H), 1.35 (d, J=7.2 Hz, 3H), 1.02 (t, J=7.6 Hz, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 189.9, 179.0, 49.3, 40.3, 24.7, 23.5, 16.3, 11.0;

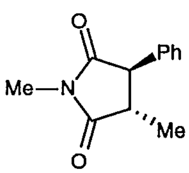
IR (neat, cm^{-1}) 2971, 2941, 2881, 1779 (shoulder), 1704, 1392, 1375, 1278;

TLC R_f 0.14 (20% ethyl acetate/hexane);

Anal. Calcd. for $C_8H_{13}N_1O_2$: C, 61.91; H, 8.44, N, 9.03. Found: C, 61.72; H, 8.25, N, 8.72;

Exact mass calcd for $C_8H_{13}N_1O_2$ (M^+) requires 155.0946 *m/z*. Found 155.0946 (EI).

Product 2d: (70%)



^{1}H NMR (R_f 0.14) ($CDCl_3$, 400 MHz) δ 7.40-7.19 (m, 5H), 3.56 (d, J=6 Hz, 1H), 3.07 (s, 3H), 2.89 (dt, J=6, 7.2 Hz, 1H), 1.42 (d, J=7.2 Hz, 3H);

^{13}C NMR (R_f 0.14) ($CDCl_3$, 100 MHz) δ 179.2, 177.0, 136.5, 129.1, 127.9, 127.7, 54.7, 44.3, 25.2, 15.3;

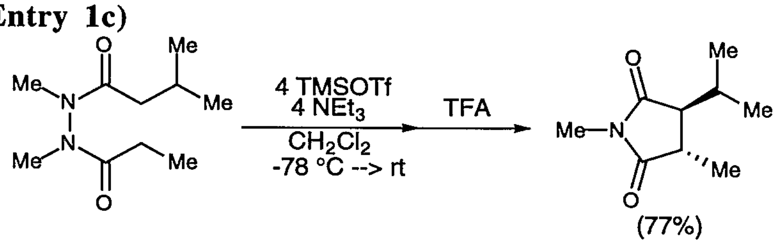
IR (R_f 0.14) (neat, cm^{-1}) 3062, 3032, 2979, 2936, 1775 (shoulder), 1698, 1457, 1436, 1388, 1276, 1137;

TLC R_f 0.14 (15% ethyl acetate/)

Anal. Calcd. for $C_{12}H_{13}N_1O_2$: C, 70.92; H, 6.45, N, 6.89. Found: C, 70.60; H, 6.63, N, 6.69;

Exact mass calcd for $C_{12}H_{14}N_1O_2$ (MH^+) requires 204.1025 *m/z*. Found 204.1021 (CI).

Method 2. (Table 1, Entry 1c)

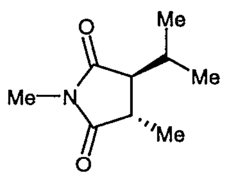


N,N'-dimethyl-*N*-*iso*-valeryl-*N'*-propanoylhydrazine (0.552 g, 2.76 mmol) was dissolved into 30 mL of anhydrous methylene chloride under Ar. The stirring solution was then chilled to -78 °C and to it was added

[2] Cartwright, D., Ving, J.L., Rinehart, Jr., K.L. *J. Am. Chem. Soc.* **1978**, *100*, 4237-4239.

trimethylsilyltrifluoromethanesulfonate (2.00 mL, 11.1 mmol). After stirring the mixture for 5 min, triethylamine (1.54 mL, 11.1 mmol) was added and the solution was stirred for an additional 30 min at -78 °C. After this period the reaction was allowed to warm to rt, and was stirred at this temp for 48 hours. After this period trifluoroacetic acid (2.13 mL, 27.6 mmol) was added to the reaction, and the mixture was stirred for 30 min. The solution was then evaporated *in vacuo* and purified directly via flash silica chromatography (10% ethyl acetate/hexane) to yield a clear liquid (0.362 g, 77 %). (R_f 0.23 in 20% ethyl acetate/hexane - stained w/$KMnO_4$)

Product 2c: (77%)



^1H NMR ($CDCl_3$, 400 MHz) δ 2.97 (s, 3H), 2.57 (dq, J=7.2, 4.0 Hz, 1H), 2.34 (m, 2H), 1.34 (d, J=7.2 Hz, 3H), 1.02 (d, J=6.8 Hz, 3H), 0.89 (d, J=6.4 Hz, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 180.1, 178.6, 43.1, 36.7, 28.6, 24.7, 29.9, 18.0, 17.3, 15.0;

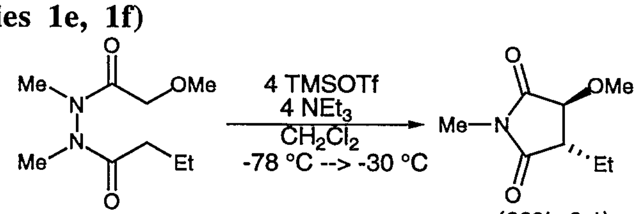
IR (neat, cm^{-1}) 2962, 2936, 2873, 1774 (shoulder), 1699, 1439, 1391, 1375, 1279;

TLC R_f 0.23 (20% ethyl acetate/hexane);

Anal. Calcd. for $C_9H_{15}N_1O_2$: C, 63.88; H, 8.93, N, 8.28. Found: C, 63.77; H, 8.95, N, 8.06;

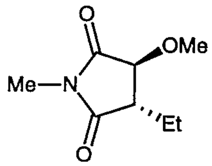
Exact mass calcd for $C_9H_{16}N_1O_2$ (MH^+) requires 170.1181 *m/z*. Found 170.1183 (CI).

Method 3. (Table 1, Entries 1e, 1f)



N,N'-dimethyl-*N*-methoxyacetyl-*N'*-propanoylhydrazide (0.34 g, 1.68 mmol) was dissolved into 15 mL of anhydrous methylene chloride under Ar. The stirring solution was then chilled to -78 °C and to it was added trimethylsilyltrifluoromethanesulfonate (1.22 mL, 6.74 mmol). After stirring the mixture for 5 min, triethylamine (0.94 mL, 6.74 mmol) was added and the solution was stirred for an additional 30 min at -78 °C. After this period the reaction was allowed to warm to -30 °C, and was stirred at this temp for 18 hours. The solution was then evaporated *in vacuo* at 0 °C and was purified directly via flash silica chromatography (20% ethyl acetate/hexane) to yield a clear liquid (0.173 g, 60%).

Product 2e: (60%)



^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.85 (d, J=4.4 Hz, 1H), 3.66 (s, 3H), 2.97 (s, 3H), 2.63 (m, 1H), 1.96 (m, 1H), 1.67 (m, 1H), 1.03 (t, J=7.6 Hz, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 176.6, 175.5, 79.9, 59.2, 48.5, 24.5, 22.2, 11.1;

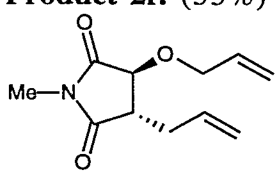
IR (neat, cm^{-1}) 2967, 2940, 1788 (shoulder), 1710, 1434, 1389, 1280, 1139, 1114, 1103, 1061;

TLC R_f 0.21 (20% ethyl acetate/hexane);

Anal. Calcd. for $C_8H_{13}N_1O_3$: C, 56.13; H, 7.65, N, 8.18. Found: C, 56.15; H, 7.75, N, 8.06;

Exact mass calcd for $C_8H_{14}N_1O_3$ (MH^+) requires 172.0974 *m/z*. Found 172.0971 (CI).

Product 2f: (53%)



^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.92 (m, 1H), 5.74 (m, 1H), 5.35 (d, J=16.4 Hz, 1H), 5.26 (d, J=10.4 Hz, 1H), 5.19 (d, J=14.4 Hz, 1H), 5.16 (d, J=9.2 Hz, 1H), 4.49 (dd, J^1=13.2 Hz, J^2=6.4 Hz, 1H), 4.28 (dd, J^1=12.8 Hz, J^2=6.4 Hz, 1H), 4.08 (d, J=4.4 Hz, 1H), 2.99 (s, 3H), 2.85 (m, 1H), 2.64 (m, 1H), 2.49 (m, 1H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 176.1, 175.6, 133.6, 133.2, 119.0, 118.5, 76.4, 72.3, 47.1, 32.7, 24.6;

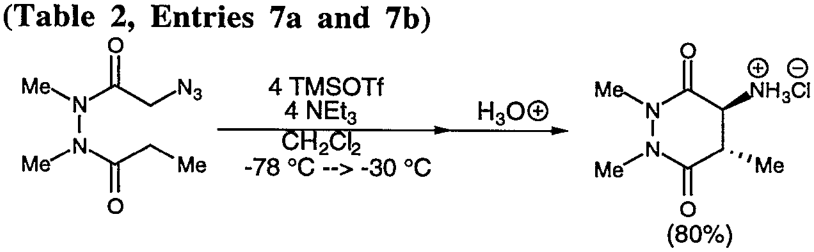
IR (neat, cm^{-1}) 2920, 1712, 1442, 1385, 1280;

TLC R_f 0.24 (20% ethyl acetate/hexane);

Anal. Calcd. for $C_{11}H_{15}NO_3$: C, 63.14; H, 7.23, N, 6.69. Found: C, 62.96; H, 7.31, N, 6.62;

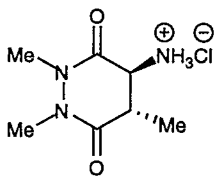
Exact mass calcd for $C_{11}H_{16}NO_3$ (MH^+) requires 210.1130 *m/z*. Found 210.1130 (CI).

Method for azides. (Table 2, Entries 7a and 7b)



N,N'-dimethyl-*N*-azidolacetyl-*N'*-propanoylhydrazide (0.231 g, 1.16 mmol) was dissolved into 12 mL of anhydrous methylene chloride under Ar. The stirring solution was then chilled to -78 °C and to it was added trimethylsilyltrifluoromethanesulfonate (0.84 mL, 4.64 mmol). After stirring the mixture for 5 min, triethylamine (0.65 mL, 4.66 mmol) was added and the solution was stirred for an additional 30 min at -78 °C. After this period the reaction was allowed to warm to -30 °C, and was stirred at this temp for 16 hours. The reaction mixture was then combined with 30mL of methylene chloride and was vigorously washed with saturated sodium bicarbonate (3x15mL). The organic layer was then dried over anhydrous sodium sulfate and evaporated *in vacuo* to yield a crude residue the bis-(trimethylsilyl)amide. This material was stirred in 10 mL of 1N hydrochloric acid for 30 min. The resulting solution was washed with methylene chloride and the aqueous layer was evaporated *in vacuo* to yield a yellowish solid (0.193g, 80%).

Product 5a: (80%)



^{1}H NMR (d6-DMSO, 400 MHz) δ 8.78 (br s, 3H), 4.19 (br d, J=13.2 Hz, 1H), 3.21 (s, 3H), 3.15 (s, 3H), 2.97 (dq, J=13.2, 6.8 Hz), 1.14 (d, J=6.8 Hz, 3H);

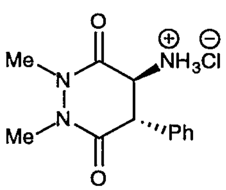
^{13}C NMR (d6-DMSO, 100 MHz) δ 168.0, 165.2, 50.5, 40.3, 36.0, 32.8, 32.6, 11.7;

IR (KBr, cm^{-1}) 3421, 2920, 2600, 2118, 1674, 1586, 1496, 1460, 1386, 1295, 1270, 1153;

Anal. Calcd. for $C_{12}H_{21}N_3O_4$ (Reported for the corresponding *t*-Butoxycarbonyl-protected compound): C, 53.12; H, 7.80, N, 15.49. Found: C, 52.83; H, 7.81, N, 15.13;

Exact mass calcd for $C_7H_{14}N_3O_2$ (M^+) requires *m/z* 172.1086. Found 172.1090 (CI).

Product 5b: (58%)



^{1}H NMR (d6-DMSO, 400 MHz) δ 8.39 (broad s, 3H), 7.37-7.28 (m, 5H), 4.91 (broad d, J=13.6 Hz, 1H), 4.26 (s, J=13.6 Hz, 1H), 3.30 (s, 3H), 3.22 (s, 3H);

^{13}C NMR (d6-DMSO, 100 MHz) δ 166.2, 164.6, 132.5, 130.5, 128.3, 128.0, 49.9, 47.4, 32.8, 32.7;

IR (KBr, cm^{-1}) 3413, 2935, 1678, 1589, 1496, 1459, 1388, 1360, 1271, 1156;

TLC (bis-(trimethylsilyl)amide) R_f 0.13 (20% ethyl acetate/hexane)

Anal. Calcd. for $C_{17}H_{23}N_3O_4$ (Reported for the corresponding *t*-Butoxycarbonyl-protected compound): C, 61.25; H, 6.95, N, 12.60. Found: C, 61.13; H, 7.13, N, 11.79;

Exact mass calcd for $C_{12}H_{16}N_3O_2$ (M^+) requires *m/z* 234.1243. Found 234.1243 (EI).