Supporting Information for

Reactions of a Carbamoylstannane with Acid Chlorides: Highly Efficient Synthesis of α -Oxo Amides

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Experimental Details

All the reactions were carried out under nitrogen atmosphere. Benzene was distilled from calcium hydride. ^1H -, ^{13}C -NMR spectra were obtained on a Bruker ARX-300 spectrometer (300 MHz for ^1H and 75 MHz for ^{13}C) in CDCl_3 and referenced to SiMe_4 (^1H), and appropriate solvent resonances (^{13}C). ^{19}F -NMR spectra (469.6 MHz) were recorded in CDCl_3 on a JEOL LA500 spectrometer and referenced to benzotrifluoride. Infrared spectra were measured on a JASCO FT/IR-5000 spectrometer. GC-MS was carried out on a Shimadzu GC-17A/QP-5000 mass spectrometer (EI, 70 eV). High resolution MS was obtained using a JEOL MS-BU20 spectrometer (EI). All the acid chlorides are commercial products and used as received. (*N,N*-diisopropylcarbamoyl)trimethylstannane **1** was prepared by the literature method.¹

A typical procedure for the reaction of carbamoylstannane with acid chlorides. At room temperature, to a solution of (*N,N*-diisopropylcarbamoyl)trimethylstannane (**1**, 1.1 mmol) and docosane (0.37 mmol, as an internal standard for GLC analysis) in 2.0 mL benzene was added 1.0 mmol of acetyl chloride by a macro-syringe over 10 min and the resulting solution was stirred at room temperature for 1 h. The GLC analysis of the reaction mixture revealed that acetyl chloride was almost completely consumed (> 99 %) and that the product *N,N*-diisopropyl-2-oxo-propionamide **3a** was formed in 96% yield. After removal of the volatiles in vacuo, the residue was subjected to column chromatography on silica gel using hexane and then CH_2Cl_2 as the eluting solvent. **3a** was obtained as a colorless oil (142.0 mg, 0.83 mmol, 83% yield).

***N,N*-Diisopropyl-2-oxopropionamide 3a.** Colorless oil, isolated yield: 83%, bp 100 °C. ^1H NMR (CDCl_3) δ 3.72 (hept, 1H, J = 6.6 Hz), 3.51 (hept, 1H, J = 6.8 Hz), 2.35 (s, 3H), 1.42 (d, 6H, J = 6.8 Hz), 1.20 (d, 6H, J = 6.6 Hz). ^{13}C NMR (CDCl_3) δ 198.8, 167.4, 49.7, 45.9, 27.3, 20.8. IR (neat) 2976, 2942, 1715, 1686, 1450, 1375, 1199 cm^{-1} . GCMS m/z (% relative intensity) 171 (M^+ , 0.5), 128 (31), 86 (100), 58 (11). Anal. Calcd for $\text{C}_9\text{H}_{11}\text{NO}_2$: C, 63.16; H, 9.94; N, 8.19. Found: C, 62.62; H, 10.0; N, 7.91.

***N,N*-Diisopropyl-3-methyl-2-oxobutyramide 3b.** Colorless oil, isolated yield: 87%, bp 30 °C (0.15 Torr). ¹H NMR (CDCl₃) δ 3.64 (hept, 1H, *J* = 6.6 Hz), 3.45 (hept, 1H, *J* = 7.0 Hz), 3.08 (hept, 1H, *J* = 6.8 Hz), 1.44 (d, 6H, *J* = 6.8 Hz), 1.18 (d, 6H, *J* = 7.0 Hz), 1.14 (d, 6H, *J* = 6.6 Hz). ¹³C NMR (CDCl₃) δ 204.5, 167.7, 49.8, 45.9, 37.3, 20.6, 20.1, 16.8. IR (neat) 2976, 2940, 2878, 1709, 1634, 1448, 1373, 1021 cm⁻¹. GCMS *m/z* (% relative intensity.) 199 (M⁺, 0.7), 128 (25), 86 (100), 71 (7). Anal. Calcd for C₁₁H₂₁NO₂: C, 66.33; H, 10.55; N, 7.03. Found: C, 65.98; H, 10.66; N, 6.70.

***N,N*-Diisopropyl-2-oxo-3-phenylpropionamide 3c.** Colorless oil, isolated yield: 72%, bp 70 °C (0.15 Torr). ¹H NMR (CDCl₃) δ 7.35–7.24 (m, 5H), 3.98 (s, 2H), 3.42–3.23 (m, 2H), 1.35 (d, 6H, *J* = 6.8 Hz), 0.80 (d, 6H, *J* = 6.6 Hz). ¹³C NMR (CDCl₃) δ 197.5, 166.8, 131.5, **130.1**, 128.9, 127.5, 50.0, 47.2, 45.8, 20.1, 19.9. IR (neat) 2976, 2938, 2878, 1711, 1636, 1450, 1373, 1212, 1036, 702, 584 cm⁻¹. GCMS *m/z* (% relative intensity.) 247 (M⁺, 1), 128 (31), 100 (1), 91 (32), 86 (100), 58 (3). Anal. Calcd for C₁₅H₂₁NO₂: C, 72.87; H, 8.50; N, 5.66. Found: C, 72.63; H, 8.83; N, 5.19. HRMS. Calcd for C₁₅H₂₁NO₂: 247.1571. Found: 247.1572.

***N,N*-Diisopropyl-3-methyl-2-oxo-3-butenamide 3d.** Colorless oil, isolated yield: 72%, bp 40 °C (0.15 Torr). ¹H NMR (CDCl₃) δ 6.08 (s, 1H), 5.96 (s, 1H), 3.57–3.42 (m, 2H), 1.92 (s, 3H), 1.48 (d, 6H, *J* = 6.8 Hz), 1.17 (d, 6H, *J* = 6.6 Hz). ¹³C NMR (CDCl₃) δ 193.6, 166.9, 141.6, 130.8, 50.1, 45.9, 20.3, 20.1, 15.8. IR (neat) 2978, 2940, 1676, 1636, 1458, 1375, 1035 cm⁻¹. GCMS *m/z* (% relative intensity.) 197 (M⁺, 0.8), 128 (37), 86 (100), 69 (25). Anal. Calcd for C₁₁H₁₉NO₂: C, 67.01; H, 9.65; N, 7.10. Found: C, 66.61; H, 9.70; N, 6.70.

(*E*)-*N,N*-Diisopropyl-2-oxo-4-phenyl-3-butenamide 3e. Colorless product, isolated yield: 85%, mp 97.5–98.5 (recrystallization in hexane). ¹H NMR (CDCl₃) δ 7.57–7.40 (m, 6H), 6.79 (d, 1H, *J* = 16.0 Hz), 3.78 (hept, 1H, *J* = 6.6 Hz), 3.56 (hept, 1H, *J* = 6.8 Hz), 1.53 (d, 6H, *J* = 6.8 Hz), 1.20 (d, 6H, *J* = 6.6 Hz). ¹³C NMR (CDCl₃) δ 191.5, 166.9, 148.0, 133.9, 131.2, 129.0, 128.6, 123.8, 50.1, 46.0, 20.7, 20.3. IR (neat) 3000, 2978, 2938, 1657, 1636, 1448, 1354, 1236, 1205, 980, 772, 687 cm⁻¹.

GCMS m/z (% relative intensity.) 259 (M^+ , 3), 131 (24), 128 (28), 103 (23), 86 (100), 77 (25). Anal. Calcd for $C_{16}H_{21}NO_2$: C, 74.13; H, 8.11; N, 5.40. Found: C, 74.41; H, 8.24; N, 5.37.

3-Chloro-*N,N*-Diisopropyl-2-oxopropionamide 3f. Colorless oil, isolated yield: 81%, bp 35 °C (0.15 Torr). 1H NMR ($CDCl_3$) δ 4.36 (s, 2H), 3.80 (hept, 1H, J = 6.6 Hz), 3.53 (hept, 1H, J = 6.8 Hz), 1.43 (d, 6H, J = 6.8 Hz), 1.22 (d, 6H, J = 6.6 Hz). ^{13}C NMR ($CDCl_3$) δ 191.2, 164.9, 50.2, 46.3, 45.5, 20.6, 20.0. IR (neat) 2978, 2942, 1719, 1640, 1452, 1375, 1207, 1141, 1031 cm^{-1} . GCMS m/z (% relative intensity.) 206 (M^+ , 0.3), 128 (35), 86 (100), 58 (6). Anal. Calcd for $C_9H_{16}ClNO_2$: C, 52.55; H, 7.78; N, 6.81. Found: C, 52.16; H, 7.88; N, 6.35.

***N,N*-Diisopropyl-3,3,4,4,5,5,5-heptafluoro-2-oxopentanamide 3g.** Colorless oil, isolated yield: 76%, bp 40 °C (0.15 Torr). 1H NMR ($CDCl_3$) δ 3.71–3.51 (m, 2H), 1.45 (d, 6H, J = 6.8 Hz), 1.25 (d, 6H, J = 6.6 Hz). ^{13}C NMR ($CDCl_3$) δ 180.9 (t, $^2J_{CF}$ = 32.0 Hz), 161.4, 117.6 (qt, $^1J_{CF}$ = 287.9 Hz; $^2J_{CF}$ = 34.0 Hz, $CF_3CF_2CF_2CO$), 108.9 (tt, $^1J_{CF}$ = 268.0 Hz; $^2J_{CF}$ = 34.0 Hz, $CF_3CF_2CF_2CO$), 108.5 (tm, $^1J_{CF}$ = 267.3 Hz, $CF_3CF_2CF_2CO$), 50.5, 46.7, 20.4, 19.7. ^{19}F NMR ($CDCl_3$) δ 62.3 (t, 3F, $^3J_{FF}$ = 9.1 Hz, $CF_3CF_2CF_2$), 24.3 (t, 2F, $^3J_{FF}$ = 9.1 Hz, $CF_3CF_2CF_2$), 17.1 [s(br), 2F, $CF_3CF_2CF_2$]. IR (neat) 2984, 2948, 1752, 1611, 1454, 1379, 1232, 1123 cm^{-1} . GCMS m/z (% relative intensity.) 268 (M^+ -3F, 3), 240 (4), 169 (6), 128 (39), 100 (2), 86 (100), 69 (21), 58 (4). HRMS. Calcd for $C_{11}H_{15}F_7NO_2$ (MH^+): 326.0990. Found: 326.0996.

***N,N*-Diisopropyl-2-oxo-2-phenylacetamide 3h.** Colorless product, isolated yield: 85%, mp 125.0–125.5 °C (recrystallization in hexane) (lit.: 124–126 °C).² 1H NMR ($CDCl_3$) δ 7.94–7.48 (m, 5H), 3.69 (hept, 1H, J = 6.6 Hz), 3.59 (hept, 1H, J = 6.8 Hz), 1.58 (d, 6H, J = 6.8 Hz), 1.17 (d, 6H, J = 6.6 Hz). ^{13}C NMR ($CDCl_3$) δ 191.0, 166.9, 134.4, 133.3, 129.5, 128.9, 50.2, 46.1, 20.5, 20.3. IR (neat) 2978, 1686, 1634, 1448, 1377, 1238, 750, 721 cm^{-1} . GCMS m/z (% relative intensity.) 233 (M^+ , 0.4), 128 (47), 105 (47), 86 (100), 77 (41), 51 (14). Anal. Calcd for $C_{14}H_{19}NO_2$: C, 72.01; H, 8.14; N, 6.00. Found: C, 72.05; H, 8.29; N, 5.91.

***N,N*-Diisopropyl-2-oxo-2-(*p*-tolyl)acetamide 3i.** Colorless product, isolated yield: 78%, mp 93.5–95.0 °C (recrystallization in hexane) (lit.: 54–55 °C).³ ¹H NMR (CDCl₃) δ 7.82 (d, 2H, *J* = 8.1 Hz), 7.29 (d, 2H, *J* = 8.1 Hz), 3.68 (hept, 1H, *J* = 6.6 Hz), 3.57 (hept, 1H, *J* = 6.8 Hz), 2.42 (s, 3H), 1.56 (d, 6H, *J* = 6.8 Hz), 1.16 (d, 6H, *J* = 6.6 Hz). ¹³C NMR (CDCl₃) δ 190.6, 167.1, 145.5, 130.9, 129.6, 50.1, 46.0, 21.9, 20.5, 20.3. IR (neat) 2974, 2936, 1678, 1634, 1605, 1450, 1375, 1243, 1375, 1243, 187, 756, 743 cm⁻¹. GCMS *m/z* (% relative intensity.) 248 (M⁺, 0.1), 233 (0.1), 128 (51), 119 (63), 100 (5), 91 (30), 86 (100), 62 (26). Anal. Calcd for C₁₅H₂₁NO₂: C, 72.87; H, 8.50; N, 5.66. Found: C, 72.89; H, 8.56; N, 5.50.

***N,N*-Diisopropyl-2-oxo-2-(*p*-bromophenyl)acetamide 3j.** Colorless product, isolated yield: 85%, mp 105.0–105.5 °C (recrystallization in hexane). (lit.: 104–105 °C).³ ¹H NMR (CDCl₃) δ 7.79 (d, 2H, *J* = 8.6 Hz), 7.64 (d, 2H, *J* = 8.6 Hz), 3.71–3.51 (m, 2H), 1.55 (d, 6H, *J* = 6.8 Hz), 1.16 (d, 6H, *J* = 6.6 Hz). ¹³C NMR (CDCl₃) δ 189.8, 166.3, 132.3, 132.2, 130.9, 129.8, 50.2, 46.2, 20.6, 20.2. IR (neat) 2974, 2936, 1682, 1636, 1586, 1450, 1375, 1238, 1071, 994, 762 cm⁻¹. GCMS *m/z* (% relative intensity.) 312 (M⁺, 0.5), 185 (9), 155 (7), 128 (45), 86 (100), 76 (11). Anal. Calcd for C₁₄H₁₈BrNO₂: C, 53.85; H, 5.76; N, 4.25. Found: C, 53.91; H, 5.74; N, 4.48.

***N,N*-Diisopropyl-2-(2-furyl)-2-oxo-acetamide 3k.** Colorless product, isolated yield: 76%, mp 114.0–114.5 °C (recrystallization in hexane). ¹H NMR (CDCl₃) δ 7.69 (d, 1H, *J* = 1.6 Hz), 7.25 (d, 1H, *J* = 1.8 Hz), 6.58 (m, 1H), 3.79 (hept, 1H, *J* = 6.6 Hz), 3.56 (hept, 1H, *J* = 6.8 Hz), 1.52 (d, 6H, *J* = 6.8 Hz), 1.19 (d, 6H, *J* = 6.6 Hz). ¹³C NMR (CDCl₃) δ 178.9, 165.5, 150.2, 148.3, 121.3, 112.7, 50.2, 46.1, 20.6, 20.1. IR (neat) 2980, 2940, 1661, 1642, 1460, 1286, 994 cm⁻¹. GCMS *m/z* (% relative intensity.) 223 (M⁺, 0.8), 128 (33), 100 (6), 95 (81), 86 (100), 67 (4), 58 (5). Anal. Calcd for C₁₂H₁₇NO₃: C, 64.57; H, 7.62; N, 6.27. Found: C, 64.95; H, 7.61; N, 6.17.

***N,N*-Diisopropyl-2-oxo-2-(2-thienyl)-acetamide 3l.** Colorless product, isolated yield: 70%, mp 146.0–147.0 °C (recrystallization in hexane). ¹H NMR (CDCl₃) δ 7.75–7.69 (m, 2H), 7.15 (m, 1H), 3.79 (hept, 1H, *J* = 6.6 Hz), 3.55 (hept, 1H, *J* = 6.8 Hz), 1.52 (d, 6H, *J* = 6.8 Hz), 1.16 (d, 6H, *J* = 6.6

Hz). ^{13}C NMR (CDCl_3) δ 183.7, 165.9, 140.7, 135.7, 135.4, 128.5, 50.3, 46.1, 20.5, 20.1. IR (neat) 2974, 2936, 1684, 1636, 1586, 1450, 1375, 1238, 1071, 994, 762 cm^{-1} . GCMS m/z (% relative intensity.) 239 (M^+ , 1), 128 (28), 111 (55), 86 (100), 83 (9), 58 (5). Anal. Calcd for $\text{C}_{12}\text{H}_{17}\text{NO}_2\text{S}$: C, 60.25; H, 7.11; N, 5.86; S, 13.39. Found: C, 60.32; H, 7.36; N, 5.96; S, 13.06.

Ethyl *N,N*-diisopropylloxamate 3m. Colorless oil, isolated yield: 78%, bp 40 °C (0.15 Torr). ^1H NMR (CDCl_3) δ 4.29 (q, 2H, J = 7.1 Hz), 3.67 (hept, 1H, J = 6.6 Hz), 3.48 (hept, 1H, J = 6.8 Hz), 1.43 (d, 6H, J = 6.8 Hz), 1.33 (t, 3H, J = 7.1 Hz), 1.22 (d, 6H, J = 6.6 Hz). ^{13}C NMR (CDCl_3) δ 163.4, 161.6, 61.5, 50.6, 45.9, 20.6, 20.0, 14.0. IR (neat) 2978, 2942, 1742, 1657, 1450, 1373, 1228, 1209, 1042, 1019 cm^{-1} . GCMS m/z (% relative intensity.) 201 (M^+ , 2), 186 (0.5), 172 (3), 128 (19), 100 (2), 86 (100), 70 (13), 58 (13). Anal. Calcd for $\text{C}_{10}\text{H}_{19}\text{NO}_3$: C, 59.70; H, 9.45; N, 6.96. Found: C, 59.84; H, 9.62; N, 6.90.

***N,N*-Diisopropyl-*N',N'*-dimethyloxamide 3n.** Colorless product, isolated yield: 22%, mp 84.0–84.5 °C (recrystallization in hexane). ^1H NMR (CDCl_3) δ 3.75 (hept, 1H, J = 6.6 Hz), 3.48 (hept, 1H, J = 6.8 Hz), 2.99 (s, 3H), 2.96 (s, 3H), 1.47 (d, 6H, J = 6.8 Hz), 1.21 (d, 6H, J = 6.6 Hz). ^{13}C NMR (CDCl_3) δ 165.4, 164.6, 50.5, 45.7, 37.1, 33.5, 20.8, 20.1. IR (melt) 2980, 2940, 1642, 1464, 1369, 1334 cm^{-1} . GCMS m/z (% relative intensity.) 200 (M^+ , 1), 185 (0.4), 157 (1), 128 (12), 100 (49), 86 (100), 72 (93), 58 (15). Anal. Calcd for $\text{C}_{10}\text{H}_{20}\text{N}_2\text{O}_2$: C, 60.00; H, 10.00; N, 14.00. Found: C, 60.25; H, 10.13; N, 13.78.

Ethyl 3-(*N,N*-diisopropylamino)-2,3-dioxopropionate 3p. Colorless product, isolated yield: 39%, mp 79.0–80.0 °C (recrystallization in hexane). ^1H NMR (CDCl_3) δ 4.28 (q, 2H, J = 7.1 Hz), 3.94 (hept, 1H, J = 6.6 Hz), 3.47 (hept, 1H, J = 6.8 Hz), 1.42 (d, 6H, J = 6.8 Hz), 1.32 (t, 3H, J = 7.1 Hz), 1.14 (d, 6H, J = 6.6 Hz). ^{13}C NMR (CDCl_3) δ 179.8, 170.3, 160.2, 63.1, 50.1, 46.3, 20.5, 19.9, 13.9. IR (neat) 2978, 2946, 1742, 1647, 1421, 1379, 1292, 1261, 1145, 1129, 1089, 1040, 592 cm^{-1} . GCMS m/z (% relative intensity.) 229 (M^+ , 0.1), 201 (0.1), 128 (38), 86 (100), 70 (6), 58 (4). HRMS. Calcd for $\text{C}_{11}\text{H}_{20}\text{NO}_4$ (MH^+): 230.1391. Found: 230.1393.

***N,N,N',N'*-Tetraisopropyl-3,3,4,4,5,5-hexafluoro-2,6-dioxopimelamide 4.** Colorless oil, isolated yield: 60%, bp 85 °C (0.15 Torr). ^1H NMR (CDCl_3) δ 3.67 (hept, 1H, $J = 6.6$ Hz), 3.56 (hept, 1H, $J = 6.8$ Hz), 1.46 (d, 6H, $J = 6.8$ Hz), 1.24 (d, 6H, $J = 6.6$ Hz). ^{13}C NMR (CDCl_3) δ 181.6 (t, $^2J_{\text{CF}} = 32.0$ Hz), 161.5, 110.1 (tquint, $^1J_{\text{CF}} = 267.0$ Hz; $^2J_{\text{CF}} = 34.0$ Hz), 109.6 (tt, $^1J_{\text{CF}} = 270.0$ Hz; $^2J_{\text{CF}} = 34.0$ Hz), 50.4, 46.6, 20.5, 19.8. ^{19}F NMR (CDCl_3) δ 26.1 (s(br), 2F), 22.1 (s(br), 2F). IR (neat) 2982, 2944, 1750, 1657, 1475, 1452, 1377, 1348, 1209, 1183, 1139 cm^{-1} . GCMS m/z (% relative intensity.) 424 ($\text{M}^+ - 2\text{F}$, 1), 334 (0.6), 264 (3), 216 (2), 128 (55), 86 (100), 70 (4), 58 (4). HRMS. Calcd for $\text{C}_{19}\text{H}_{28}\text{F}_6\text{N}_2\text{O}_4$: 462.1951. Found: 462.1958.

***N,N,N',N'*-Tetraisopropyl-2,3-dioxosuccinamide 5.** Colorless product, isolated yield: 72%, mp 88.0–89.5 °C (recrystallization in hexane). ^1H NMR (CDCl_3) δ 4.11 (hept, 1H, $J = 6.6$ Hz), 3.53 (hept, 1H, $J = 6.8$ Hz), 1.44 (d, 6H, $J = 6.8$ Hz), 1.26 (d, 6H, $J = 6.6$ Hz). ^{13}C NMR (CDCl_3) δ 181.6, 166.2, 50.4, 46.0, 20.6, 20.1. IR (neat) 2976, 2942, 1717, 1636, 1458, 1365, 735, 592 cm^{-1} . GCMS m/z (% relative intensity.) 312 (M^+ , 0.3), 213 (3), 128 (30), 100 (2), 86 (100), 70 (4), 58 (3). HRMS. Calcd for $\text{C}_{15}\text{H}_{28}\text{N}_2\text{O}_3$ ($\text{M}^+ - \text{CO}$): 284.2098. Found: 284.2099.

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