Supporting Imformation

Efficient synthesis of β-oxopropylcarbamates in compressed CO_2 without any additional catalyst and solvent

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General imformation. IR spectra were obtained with a Tensor-27 FTIR spectrometer. ^{1}H and ^{13}C spectra were recorded on a Bruker DRX-400 with tetramethylsilane as the internal standard and $CDCl_3$ as solvent. GC-MS data were recorded on a HP 6890-5973 spectrometer. All the propargyl alcohols were purchased from Aldrich and used without further purification. Secondary amines were dried with conventional method before use.

Analytical data of the products.

1,1-Dimethyl-2-oxopropyl N, N-diethylcarbamate (3a):

IR(neat): v = 2980, 2937, 1696, 1475, 1425, 1377, 1284, 1159, 1124, 1062, 1026, 978, 915, 775, 691, 590, 510 cm^{-1}. MS (EI): *m/z* =201 (M+), 186, 177, 158, 143, 116, 100, 86, 72, 57, 43, 27. ^{1}H NMR (400 MHz, TMS, $CDCl_3$): δ = 1.10(t, J = 6.8 Hz, 6H, CH_3), 1.41 (s, 6H, CH_3), 2.08(s, 3H, CH_3), 3.25 (t, J = 6.8 Hz, 4H, CH_2). ^{13}C NMR (400 MHz, TMS, $CDCl_3$): δ = 13.5, 14.1, 41.6, 82.8, 154.6, 207.7.

1-methyl-1-phenyl-2-oxopropyl N, N-diethylcarbamate (3b):

IR(neat): v = 3061, 2977, 2936, 2877, 1700, 1601, 1476, 1368, 1281, 1224, 1169, 1101, 1074, 1029, 977, 764, 700, 561, 520. cm^{-1}. MS (EI): *m/z* =263 (M+), 221, 187, 162, 147, 132, 100, 91, 72, 58, 43, 27. ^{1}H NMR (400 MHz, TMS, $CDCl_3$): δ = 1.16(t, J = 7.2 Hz, 3H, CH_3), 1.28(t, J = 7.2 Hz, 3H, CH_3), 1.77(s, 3H, CH_3), 1.94(s, 3H, CH_3), 3.34(q, J = 7.2 Hz, 2H), 3.47(q, J = 7.2 Hz, 2H), 7.29-7.42(m, 5H, C_6H_5). ^{13}C NMR (400 MHz, TMS, $CDCl_3$): δ = 13.5, 14.3, 23.6, 42.0, 86.9, 124.6, 127.8, 128.6, 139.6, 154.2, 208.0. Anal. Calcd for $C_{15}H_{21}NO_3$: C, 68.42; H, 8.04; N, 5.32. Found: C, 68.28; H, 8.42; N,

4.76.

1-methyl-1-n-hexyl-2-oxopropyl N, N-diethylcarbamate (3c):

IR(neat): v = 2933, 2860, 1697, 1476, 1424, 1378, 1351, 1316, 1282, 1255, 1171, 1126, 1096, 978, 771, 726 cm^{-1}. MS (EI): *m/z* =271 (M+), 256, 228, 187, 177, 153, 139, 116, 100, 85, 72, 58, 43, 27. ^{1}H NMR (400 MHz, TMS, $CDCl_3$): δ = 0.85(t, J = 4.4 Hz, 3H), 1.07-1.16(m, 6H, CH_3), 1.20-1.26(m, 8H, CH_2), 1.45 (s, 3H, CH_3), 1.59-1.81(m, 2H, CH_2), 2.09(s, 3H, CH_3), 3.21-3.30 (m, 4H, CH_2). ^{13}C NMR (400 MHz, TMS, $CDCl_3$): δ = 13.5, 14.0, 14.1, 20.3, 22.5, 23.1, 23.9, 29.4, 31.5, 36.7, 41.6, 85.3, 154.5, 208.0.

1-acetylcyclohexyl diethylcarbamate (3d):

IR(neat): v = 2974, 2937, 2962, 1697, 1540, 1451, 1350, 1316, 1290, 1254, 1226, 1201, 1173, 1140, 1059, 984, 928, 847, 771, 632, 600, 499, 472 cm^{-1}. MS (EI): *m/z* =241 (M+), 226, 198, 173, 154, 143, 126, 116, 100, 84, 72, 58, 43, 27. ^{1}H NMR (400 MHz, TMS, $CDCl_3$): δ = 1.10(t, J = 7.2 Hz, 3H, CH_3), 1.19(t, J = 7.2 Hz, 3H, CH_3), 1.43-1.65(m, 8H, CH_2), 2.02-2.05(m, 2H, CH_2), 2.08(s, 3H, CH_3), 3.26(q, J = 7.2, 2H, CH_2), 3.33(q, J = 7.2, 2H, CH_2). ^{13}C NMR (400 MHz, TMS, $CDCl_3$): δ = 13.5, 14.3, 21.5, 23.5, 25.2, 31.1, 41.6, 41.7, 84.3, 154.4, 208.2. Anal. Calcd for $C_{13}H_{23}NO_3$: C, 64.70; H, 9.61; N, 5.80. Found: C, 63.83; H, 9.78; N, 5.42.

1,1-Dimethyl-2-oxopropyl N, N-tetramethylenecarbamate (3e):

IR(neat): v = 2981, 2860, 1770, 1539, 1414, 1354, 1161, 1124, 1095, 1029, 969, 924, 865, 825, 771, 724, 583, 509 cm^{-1}. MS (EI): *m/z* =199 (M+), 184, 156, 139, 114, 98, 70, 55, 41, 26. ^{1}H NMR (400 MHz, TMS, $CDCl_3$): δ = 1.44(s, 6H, CH_3), 1.84-1.88(m, 4H, CH_2), 2.13(s, 3H, CH_3), 3.33-3.39(m, 4H, CH_2). ^{13}C NMR (400 MHz, TMS, $CDCl_3$): δ = 23.6, 24.9, 25.7, 82.7, 153.8, 208.0.

1-methyl-1-phenyl-2-oxopropyl N, N-tetramethylenecarbamate (3f):

IR(neat): v = 2977, 2862, 1722, 1696, 1415, 1350, 1236, 1177, 1132, 1025, 767, 708, 562 cm^{-1}. MS (EI): *m/z* =261 (M+), 219, 174, 160, 147, 132, 116, 98, 77, 55, 41, 27. ^{1}H NMR (400 MHz, TMS, $CDCl_3$): δ = 1.77(s, 3H, CH_3), 1.90 (s, 3H, CH_3), 1.92-2.05(m, 4H, CH_2), 3.34-3.38 (m, 2H, CH_2), 3.59-3.71(m, 2H, CH_2), 7.32-7.50(m, 5H, C_6H_5). ^{13}C NMR (400 MHz, TMS, $CDCl_3$): δ = 23.6, 24.1, 25.5, 26.4, 46.8, 87.1, 125.6, 128.6, 129.4, 140.9, 153.8, 204.1. Anal. Calcd for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36. Found: C, 69.02; H, 7.74; N, 4.97.

1-methyl-1-n-hexyl-2-oxopropyl N, N-tetramethylcarbamate (3g):

IR(neat): v = 2933, 2860, 1697, 1476, 1424, 1378, 1351, 1316, 1282, 1255, 1171, 1126, 1096, 978, 771, 726 cm^{-1}. MS (EI): *m/z* =255 (M+), 226, 198, 185, 171, 158, 142, 126, 114, 98, 69, 55, 41, 26. ^{1}H NMR (400 MHz, TMS, $CDCl_3$): δ = 0.85(t, J = 6.8 Hz, 3H, CH_3), 1.20-1.25(m, 8H, CH_2), 1.47(s, 3H, CH_3), 1.58-1.64(m, 2H, CH_2), 1.80-1.90(m, 4H, CH_2), 2.11(s, 3H, CH_3), 3.33-3.40(m, 4H, CH_2). ^{13}C NMR (400 MHz, TMS, $CDCl_3$): δ = 13.9, 20.4, 22.4, 24.1, 25.6, 29.3, 31.5, 36.7, 45.9, 85.1, 153.6, 208.1.

1-acetylcyclohexyl N, N-tetramethylcarbamate (3h):

IR(neat): v = 2974, 2938, 2895, 2862, 1690, 1545, 1450, 1410, 1250, 1225, 1180, 1142, 1120, 1095, 1049, 1029, 970, 943, 861, 773, 553. cm^{-1}. MS (EI): *m/z* =239 (M+),213, 196, 169, 141, 126, 114, 98, 70, 55, 41, 26. ^{1}H NMR (400 MHz, TMS, $CDCl_3$): δ = 1.23-1.25(m, 2H, CH_2), 1.53-1.60(m, 8H, CH_2), 1.87-1.92 (m, 4H, CH_2), 2.02 (s, 3H, CH_3), 3.28(t, J = 6.4 Hz, 2H, CH_2), 3.49(t, J = 6.4 Hz, 2H, CH_2). ^{13}C NMR (400 MHz, TMS, CD_3COCD_3): δ = 22.1, 23.5, 25.5, 25.9, 26.4, 31.6, 46.7, 84.5, 154.0, 207.6. Anal. Calcd for $C_{13}H_{21}NO_3$: C, 65.25; H, 8.84; N, 5.85. Found: C, 65.10; H, 9.26; N, 5.52.

1,1-Dimethyl-2-oxopropyl N, N-tetramethylenecarbamate (3i):

IR(neat): v = 2985, 2926, 2858, 1699, 1427, 1362, 1301, 1277, 1255, 1158, 1119, 1023, 916, 855, 768, 586, 509. cm^{-1}. MS (EI): *m/z* =215 (M+), 201, 172, 157, 130, 114, 100, 86, 70, 57, 41, 27. ^{1}H NMR (400 MHz, TMS, $CDCl_3$): δ = 1.46(s, 3H, CH_3), 1.53 (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 3.45-3.48(m, 4H, CH_2), 3.49(m, 4H, CH_2). ^{13}C NMR (400 MHz, TMS, $CDCl_3$): δ = 23.6, 43.7, 44.6, 66.6, 83.4, 154.1, 207.2. Anal. Calcd for $C_{13}H_{21}NO_3$: C, 55.80; H, 7.96; N, 6.51. Found: C, 56.16; H, 8.32; N, 6.15.