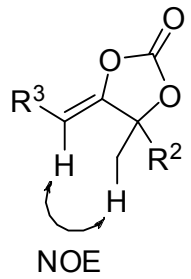
Eur. J. Org. Chem. **2007** · © WILEY-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, 2007 · ISSN 1434–193X

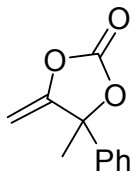
SUPPORTING INFORMATION

Title: Silver-Catalyzed Incorporation of Carbon Dioxide into Propargylic Alcohols
Author(s): Wataru Yamada, Yudai Sugawara, Hau Man Cheng, Taketo Ikeno, Tohru Yamada*
Ref. No.: O200700169

Spectroscopic data for carbonates 2a-n

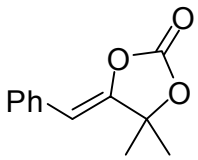
In NOE experiments, a correlation between the olefinic proton and the methyl or methylene protons bound to the C-4 carbon on the 5-alkylidene-4,4-disubsti--tuted-1,3-dioxolan-2-one ring of the products (**2c**, **2d**, **2e**, **2f**, **2g**, **2h**, **2i**, **2j**, **2l**, **2m**, **2n**) was detected, respectively. The intensities (%) of signal were indicated.





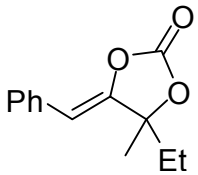
2a

4-Methyl-5-methylene-4-phenyl-1,3-dioxolan-2-one: Colorless liquid. ^{1}H NMR (400 MHz $CDCl_3$): δ 1.90 (s, 3H), 4.39 (d, 1H, *J* = 3.9 Hz), 4.87 (d, 1H, *J* = 3.9 Hz), 7.28-7.46 (m, 5H); ^{13}C NMR (100 MHz $CDCl_3$): δ 27.5, 87.1, 88.1, 124.6, 128.8, 129.1, 139.1, 151.0, 157.3; IR (NaCl) 2925, 1827, 1682, 1225, 1062, 1021, 862 cm^{-1}. Found: C, 69.35; H, 5.35%. Calcd for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30%.



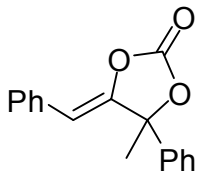
2b

(*Z*)-5-Benzylidene-4,4-dimethyl-1,3-dioxolan-2-one: ^{1}H NMR (400 MHz $CDCl_3$): δ 1.69 (s, 6H), 5.50 (s, 1H), 7.23-7.57 (m, 5H); ^{13}C NMR (100 MHz $CDCl_3$): δ 27.8, 85.5, 101.5, 127.5, 128.3, 128.6, 132.3, 150.6, 151,2; IR (NaCl) 2984, 1812, 1701, 1282, 1231, 1148, 1055, 1017, 765 cm^{-1}. m.p. 42.1–44.0 °C. HRMS: Calcd for $C_{12}H_{12}O_3$: M^+ = 204.0786. Found: *m*/*z* 204.0786.



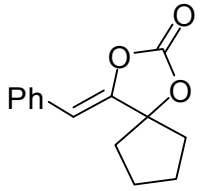
2c

(*Z*)-5-Benzylidene-4-ethyl-4-methyl-1,3-dioxolan-2-one: Colorless liquid. ^{1}H NMR (400 MHz $CDCl_3$): δ 0.95 (t, 3H, *J* = 7.3 Hz), 1.59 (s, 3H), 1.78 (dq, 1H, *J* = 14.6, 7.3 Hz), 1.93 (dq, 1H, *J* = 14.6, 7.3 Hz), 5.38 (s, 1H), 7.16-7.50 (m, 5H); ^{13}C NMR (100 MHz $CDCl_3$): δ 7.5, 26.1, 33.8, 88.4, 101.8, 127.5, 128.4, 128.5, 132.3, 149.4, 151.5; IR (NaCl) 2924, 1828, 1698, 1222, 1042, 766, 693 cm^{-1}. HRMS: Calcd for $C_{13}H_{14}O_3$: M^+ = 18.0943. Found: *m*/*z* 218.0962; NOE: 2.2 %.



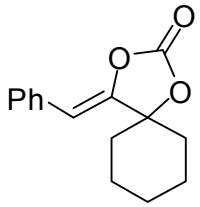
2d

(*Z*)-5-Benzylidene-4-methyl-4-phenyl-1,3-dioxolan-2-one: ^{1}H NMR (400 MHz $CDCl_3$): δ 2.06 (s, 3H), 5.91 (s, 1H), 7.22-7.61 (m, 10H); ^{13}C NMR (100 MHz $CDCl_3$): δ 27.2, 87.9, 104.3, 124.9, 127.7, 128.5, 128.6, 128.9, 129.2, 132.1, 139.3, 149.4, 151.5; IR (KBr) 1821, 1698, 1042, 1001, 763, 694 cm^{-1}. m.p. 77.7–78.2 °C. Found: C, 76.49; H, 5.34%. Calcd for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30%. NOE: 1.0 %.



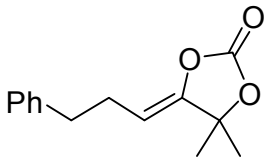
2e

(*Z*)-4-Benzylidene-1,3-dioxaspiro[4,4]nonan-2-one: ^{1}H NMR (400 MHz $CDCl_3$): δ 1.76-2.02 (m, 6H), 2.16-2.30 (m, 2H), 5.46 (s, 1H), 7.14-7.54 (m, 5H); ^{13}C NMR (100 MHz $CDCl_3$): δ 24.4, 40.9, 95.2, 101.6, 127.4, 128.3, 128.5, 132.4, 149.6, 151.4; IR (KBr) 2978, 1811, 1703, 1233, 1046, 754, 696 cm^{-1}. m.p. 89.4–92.4 °C. HRMS: Calcd for $C_{14}H_{14}O_3$: M^+ = 230.0943. Found: *m*/*z* 230.0920. NOE: 14.3 %.



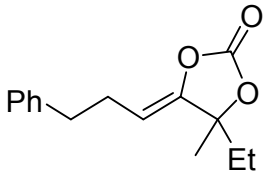
2f

(*Z*)-4-Benzylidene-1,3-dioxaspiro[4,5]decan-2-one: ^{1}H NMR (400 MHz $CDCl_3$): δ 1.20-2.15 (m, 10H), 5.47 (s, 1H), 7.22-7.60 (m, 5H); ^{13}C NMR (100 MHz $CDCl_3$): δ 21.8, 24.5, 36.7, 87.3, 101.7, 127.4, 128.4, 128.5, 132.5, 150.8, 151.4; IR (KBr) 2936, 1812, 1703, 1211, 1046, 692 cm^{-1}. m.p. 144.1–145.6 °C. HRMS: Calcd for $C_{15}H_{16}O_3$: M^+ = 244.1099. Found: *m*/*z* 244.1119. NOE: 7.1 %.



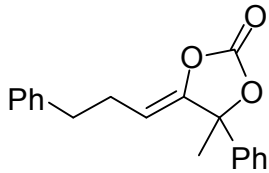
2g

(*Z*)-4,4-Dimethyl-5-(3-phenyl-propylidene)-1,3dioxolan-2-one: ^{1}H NMR (400 MHz $CDCl_3$): δ 1.51 (s, 6H), 2.46 (q, 2H, *J* = 7.3 Hz), 2.71 (t, 2H, *J* = 7.3 Hz), 4.56 (t, 1H, *J* = 7.3 Hz), 7.07-7.37 (m, 5H); ^{13}C NMR (100 MHz $CDCl_3$): δ 26.5, 27.7, 31.0, 35.3, 84.3, 100.5, 126.0, 128.2, 128.3, 140.7, 151.4; IR (KBr) 2932, 1815, 1720, 1245, 1142, 1026 cm^{-1}. m.p. 55.1-56.8 °C. Found: C, 72.36; H, 7.02%. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94%. NOE: 9.0 %.



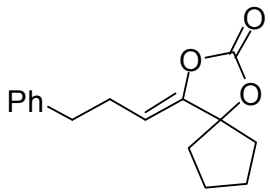
2h

(*Z*)-4-Ethyl-4-methyl-5-(3-phenylpropylidene)-1,3-dioxolan-2-one: Colorless liquid. ^{1}H NMR (400 MHz $CDCl_3$): δ 0.87 (t, 3H, *J* = 7.3 Hz), 1.49 (s, 3H), 1.64 (dq, 1H, *J* = 14.6, 7.3 Hz), 1.81 (dq, 1H, *J* = 14.6, 7.3 Hz), 2.42-2.58 (m, 2H), 2.72 (t, 2H, *J* = 7.8 Hz), 4.52 (t, 1H, *J* = 7.6 Hz), 7.15-7.33 (m, 5H); ^{13}C NMR (100 MHz $CDCl_3$): δ 7.39, 26.2, 26.5, 33.6, 35.4, 87.3, 100.9, 126.0, 128.29, 128.34, 140.8, 150.1, 151.8; IR (NaCl) 2931, 1825, 1717, 1230, 1045 cm^{-1}. HRMS: Calcd for $C_{15}H_{18}O_3$: M^+ = 246.1256. Found: *m*/*z* 246.1270. NOE: 3.0 %.



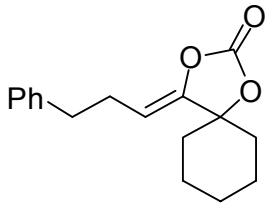
2i

(*Z*)-4-Methyl-4-phenyl-5-(3-phenylpropylidene)-1,3-dioxolan-2-one: Colorless oil. ^{1}H NMR (400 MHz $CDCl_3$): δ 1.87 (s, 3H), 2.44-2.62 (m, 2H), 2.68-2.80 (m, 2H), 4.70 (t, 1H, *J* = 7.3 Hz), 7.11-7.43 (m, 10H); ^{13}C NMR (100 MHz $CDCl_3$): δ 26.6, 27.5, 35.2, 86.9, 103.7, 124.7, 126.1, 128.3, 128.4, 128.7, 128.9, 139.6, 140.6, 150.3, 151.4; IR (NaCl) 2928, 1820, 1713, 1496, 1452, 1228, 1069, 1036, 750, 699 cm^{-1}. Found: C, 77.41; H, 6.40%. Calcd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16%. NOE: 2.5 %.



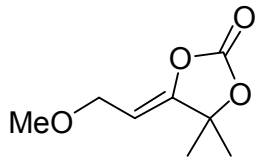
2j

(*Z*)-4-(3-Phenylpropylidene)-1,3-dioxaspiro[4,4]nonan-2-one: ^{1}H NMR (400 MHz $CDCl_3$): δ 1.72-2.22 (m, 8H), 2.48 (q, 2H, *J* = 7.3 Hz), 2.71 (t, 2H, *J* = 7.3 Hz), 4.60 (t, 1H, *J* = 7.3 Hz), 7.15-7.30 (m, 5H); ^{13}C NMR (100 MHz $CDCl_3$): δ 24.2, 26.6, 35.4, 40.7, 94.0, 100.6, 126.0, 128.2, 128.3, 140.8, 150.2, 151.6; IR (KBr) 2956, 1806, 1716, 1329, 1234, 1153, 1046, 768, 750, 701 cm^{-1}. m.p. 73.8–76.2 °C. Found: C, 74.47; H, 7.04%. Calcd for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02%. NOE: 9.0 %.



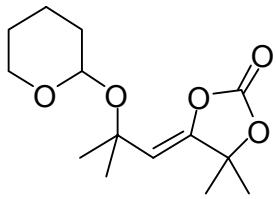
2k

(*Z*)-4-(3-Phenylpropylidene)-1,3-dioxaspiro[4.5]decan-2-one: ^{1}H NMR (400 MHz $CDCl_3$): δ 1.17-2.00 (m, 10H), 2.47 (q, 2H, *J* = 7.8 Hz), 2.70 (t, 2H, *J* = 7.8 Hz), 4.54 (t, 1H, *J* = 7.8 Hz), 7.14-7.36 (m, 5H); ^{13}C NMR (100 MHz $CDCl_3$): δ 21.7, 24.4, 26.4, 35.4, 36.7, 86.1, 100.7, 126.0, 128.2, 128.4, 140.8, 151.6, 151.7; IR (KBr) 2938, 1823, 1716, 1201, 1046, 1025 cm^{-1}. m.p. 66.0–67.2 °C. HRMS: Calcd for $C_{17}H_{21}O_3$: $(M+1)^+$ = 273.1491. Found: *m*/*z* 273.1491. Deposition number of X-ray crystal structure **2k**: CCDC 635752.



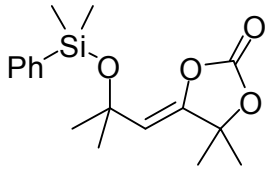
2l

(*Z*)-4-(2-Methoxyethylidene)-5,5-dimethyl-1,3-dioxolan-2-one: Colorless liquid. ^{1}H NMR (400 MHz $CDCl_3$): δ 1.62 (s, 6H), 3.33 (s, 3H), 4.07 (d, 2H, *J* = 6.8 Hz), 4.81 (t, 1H, *J* = 6.8 Hz); ^{13}C NMR (100 MHz $CDCl_3$): δ 27.6, 58.1, 65.6, 84.5, 98.0, 150.9, 153.6; IR (NaCl) 2927, 1829, 1716, 1156, 1040 cm^{-1}. Found: C, 55.51; H, 6.97%. Calcd for $C_8H_{12}O_4$: C, 55.81; H, 7.02%. NOE: 6.0 %.



2m

(*Z*)-4,4-Dimethyl-5-[2-methyl-2-(tetrahydro-2-pyranyloxy)-propylidene]-[1,3]-dioxolan-2-one: Colorless liquid. ^{1}H NMR (400 MHz $CDCl_3$): δ 1.42-1.72 (m, 17H), 1.80-1.91 (m, 1H), 3.39-3.48 (m, 1H), 3.90-4.00 (m, 1H), 4.62-4.70 (m, 1H), 4.82 (s, 1H); ^{13}C NMR (100 MHz $CDCl_3$): δ 21.0, 25.3, 27.2, 27.8, 28.5, 32.5, 63.9, 75.3, 84.9, 95.3, 107.7, 149.9, 151.24; IR (NaCl) 2941, 2869, 1834, 1712, 1261, 1163, 768 cm^{-1}. Found: C, 61.95; H, 8.21%. Calcd for $C_{14}H_{22}O_5$: C, 62.20; H, 8.20%. NOE: 5.0 %.



2n

(*Z*)-5-[2-(Dimethylphenylsilanyloxy)-2-methyl-propylidene]-4,4-dimethyl-[1,3]dioxolan-2-one: Colorless liquid. ^{1}H NMR (400 MHz $CDCl_3$): δ 0.37 (s, 6H), 1.41 (s, 6H), 1.45 (s, 6H), 4.68 (s, 1H), 7.32-7.60 (m, 5H); ^{13}C NMR (100 MHz $CDCl_3$): δ 1.09, 27.6, 31.1, 73.1, 84.7, 110.3, 127.7, 129.3, 133.2, 139.7, 148.2, 151.1; IR (NaCl) 3445, 2981, 1815, 1711, 1254, 1119, 1053 cm^{-1}. Found: C, 63.65; H, 7.55%. Calcd for $C_{17}H_{24}O_4Si$: C, 63.72; H, 7.55%. NOE: 1.0 %.