Gold and Silver-Catalyzed Highly Regioselective Addition of Active Methylenes to Dienes, Triene, and Cyclic Enol Ethers

Rene-Viet Nguyen, Xiao-Quan Yao, D. Scott Bohle,[†] and Chao-Jun Li*

Department of Chemistry, McGill University, 801 Sherbrooke St. West, Montreal, QC H3A 2K6 Canada; cj.li@mcgill.ca

Supporting information

All experiments were carried out under a nitrogen atmosphere. Dichloromethane was dried using CaH_2 . Column chromatography was performed over Sorbent silica gel 30-60 μm . ^1H -NMR spectra were acquired by Varian 400 and 100MHz or 300 and 75MHz, respectively, and referenced to the internal solvent signals. IR spectra were recorded by ABB Bomem MB100 spectrometer. Mass spectra data and HRMS were obtained by Kratos MS25RFA Mass Spectrometer. X-ray determination was resolved by Rigaku AFC63 four-circle diffractometer.

Typical experimental procedure(entry 1, table 2):

A solution of AuCl_3 (7.6 mg, 0.025 mmol) and AgOTf (19.3 mg, 0.075 mmol) was stirred in dichloromethane(2 mL) at room temperature for 2 hrs. Dibenzoylmethane(112 mg, 0.5 mmol) was then added which was followed by the addition of cyclooctadiene(128 μL , 1 mmol) via a syringe pump over 5 h and the resulting solution was stirred overnight. The solvent was removed under reduced pressure and the product was isolated via column chromatography on silica gel(gradient eluent: hexane: ethyl acetate = 60:1 to 2:1).

2-Cyclooct-2-enyl-1,3-diphenyl-propane-1,3-dione.

IR(KBr

plate): $\nu_{\max}$ 2929, 2851, 1688, 1594, 1447, 1239, 976, 776, 715 cm^{-1} ; ^1H NMR(CDCl_3 , 300MHz, ppm): δ = 8.04-7.96(m, 5H), 7.46-7.39(m, 5H), 5.63(m, 1H) 5.31-5.22(m, 2H), 3.83(m, 1H), 2.30(m,1H), 2.04(m, 1H), 1.87-1.22(m, 10H); ^{13}C NMR(CDCl_3 , 75MHz, ppm): δ = 195.5, 137.3, 133.5, 130.5, 129.0, 63.7, 38.2, 34.5, 31.3, 29.9, 27.1, 25.8; MS(EI): m/z(%) 332(M^+), 227(100), 105, 77; HRMS calc'd for $\text{C}_{23}\text{H}_{24}\text{O}_2$: 332.1776; found, 332.1771. **2-Cyclohepta-2,4-dienyl-1,3-diphenyl-propane-1,3-dione.**

IR(KBr

plate): $\nu_{\max}$ = 3008, 2915, 2352, 1696, 1647, 1595, 1442, 1269, 991, 758 cm^{-1} ; ^1H NMR(CDCl_3 , 300MHz, ppm): δ = 7.98-7.39(m, 4H), 7.55-7.40(m, 6H), 5.90(m, 2H), 5.67(m, 2H), 5.54(d, 1H, J=9.9 Hz), 3.74(m,1H), 2.42(m, 2H), 1.95(m, 2H); ^{13}C NMR(CDCl_3 , 100MHz, ppm): δ = 195.3, 194.3, 137.3, 134.6, 133.6, 131.5, 129.1, 60.6, 60.2, 42.7, 38.2, 35.0, 30.1, 30.0, 29.6; MS(EI): m/z(%) 316(M^+), 225, 211, 105(100), 77; HRMS: calc'd for $\text{C}_{22}\text{H}_{20}\text{O}_2$: 316.1463; found, 316.1459. **2-Cyclohex-2-enyl-1,3-diphenyl-propane-1,3-dione.**

IR(KBr plate):

2931, 2360, 1679, 1643, 1595, 1446, 1269, 971, 709 cm^{-1} ; ^1H NMR(CDCl_3 , 300MHz, ppm): δ = 7.99-7.97(m, 4H), 7.55(m, 2H), 7.45-7.42(m, 4H), 5.73(m, 1H), 5.52(m, 1H), 5.296(d, 1H, J=9.9Hz), 3.49(m, 1H), 2.01(m, 2H), 1.75(m, 2H), 1.37(m, 2H); ^{13}C NMR(CDCl_3 ,75MHz, ppm): δ = 201.9, 194.9, 137.3, 133.7, 132.0, 129.6, 128.7, 62.8, 37.6, 27.8, 25.5, 21.5; MS(EI): m/z(%) 304(M^+), 223, 199(100), 105, 77; HRMS: calc'd for $\text{C}_{21}\text{H}_{20}\text{O}_2$: 304.1463; found, 304.1459. **2-Cyclopent-2-enyl-1,3-diphenyl-propane-1,3-dione.**

IR(KBr plate):

2919, 1728, 1695, 1655, 1495, 1265, 987, 693 cm^{-1} ; ^1H NMR(CDCl_3 , 300MHz, ppm): δ = 8.00-7.93(m, 4H), 7.59-7.40(m, 6H), 5.58(m, 1H), 5.18(d, 1H, J=9.9Hz), 3.84(m, 1H), 2.40-2.19(m, 4H); ^{13}C NMR(CDCl_3 ,75MHz, ppm): δ = 203.5, 195.1, 133.6, 132.5, 129.1, 128.9, 62.2, 38.4, 32.1, 29.3; MS(EI): m/z(%) 223, 185(100) 105, 77; MS(ESI): m/z 290(M^+), 223; HRMS calc'd for $\text{C}_{13}\text{H}_{13}\text{O}(\text{M}^+ - \text{COPh})$: 185.0966; found, 185.0967.

1,3-Diphenyl-2-(tetrahydro-pyran-2-yl)-propane-1,3-dione.

IR(KBr plate): 2959, 1687, 1653, 1594, 1446, 1196, 1087, 711 686cm⁻¹; ¹H NMR(CDCl₃, 300MHz, ppm): δ= 7.97(m, 5H), 7.59-7.41(m, 5H), 5.48(d, 1H, J=9Hz), 4.93(m, 1H), 3.90(m, 1H), 3.45(m, 1H), 1.82(m, 2H), 1.59(m, 2H), 1.40(m, 2H); ¹³C NMR(CDCl₃, 75MHz, ppm): δ= 194.63, 193.45, 149.98, 137.51, 136.86, 133.80, 133.38, 69.27, 63.25, 36.88, 26.28, 23.71; MS(EI): m/z(%) 308, 203, 105(100), 77; HRMS calc'd for C₂₀H₁₈O₃: 308.1399; found, 308.1398.

2-(6-Methoxy-tetrahydro-pyran-2-yl)-1,3-diphenyl-propane-1,3-dione.

IR(KBr plate): 2936, 1696, 1596, 1448, 1224, 1119, 1000, 951 cm⁻¹; ¹H-NMR(CDCl₃, 300MHz, ppm): δ= 8.04-7.91(m, 4H), 7.55-7.40(m, 6H), 5.58(d, 1H, J=9.3Hz), 4.50(dt, 1H, J=9.3, 1.7Hz), 4.29(dd, 1H, J=8.5, 1.3Hz), 3.06(s, 3H), 1.83-1.76(m, 4H), 1.66(m, 2H); MS(EI): m/z(%) 233, 224, 184, 105(100), 77(100); ¹³C NMR(CDCl₃, 75MHz, ppm): δ= 194.5, 193.3, 137.7, 133.8, 129.0, 127.4, 98.7, 70.2, 63.7, 54.9, 30.2, 29.9, 18.3; MS(ESI): m/z(%) 338.1 (M⁺); HRMS calc'd for C₁₄H₁₇O₃(M⁺-COPh) : 233.11777; found, 233.11752. Another diastereoisomer: ¹H-NMR(CDCl₃, 300MHz, ppm): δ= 8.02-7.94(m, 4H), 7.56-7.40(m, 6H), 5.43(d, 1H, J=9.3Hz), 4.91(dt, 1H, J=9.3, 1.4Hz), 4.58(m, 1H), 3.14(s, 3H), 1.96-1.79(m, 3H), 1.68-1.56(m, 3H); ¹³C NMR(CDCl₃, 75MHz, ppm): δ= 194.0, 193.1, 136.9, 134.2, 130.2, 129.0, 128.6, 99.4, 70.8, 64.0, 54.1, 29.6, 29.3, 18.8.

2-(6-Ethyl-tetrahydro-pyran-2-yl)-1,3-diphenyl-propane-1,3-dione.

IR(KBr plate): 2956, 1704, 1659, 1596, 1498, 1280, 1196, 1029, 760cm⁻¹; ¹H NMR(CDCl₃, 300MHz, ppm): δ= 8.02-7.94(m, 4H), 7.54-7.40(m, 6H), 5.40(d, 1H, J=9.8Hz), 4.92(dt, 1H, J=9.8, 2.4 Hz), 4.69(m, 1H), 3.41(m, 1H), 3.16(m, 1H), 1.95-1.82(m, 2H), 1.63(m, 2H), 1.41(m, 2H), 1.11(t, 3H, J=8.1, 4.2 Hz); ¹³C NMR(CDCl₃, 75MHz, ppm): δ= 194.6, 193.4, 133.9, 133.4, 129.1, 128.8, 127.4, 102.2, 64.1, 62.4, 37.5, 30.1, 29.1, 15.4, 14.6; MS(EI): m/z(%) 247, 224, 184, 105(100), 77; MS(ESI): m/z(%) 352.1 (M⁺); HRMS calc'd for C₁₅H₁₉O₃(M⁺-COPh): 247.13342; found, 247.13299. Another diastereoisomer ¹H NMR(CDCl₃, 300MHz, ppm): δ= 8.00-7.92(m, 4H), 7.59-7.40(m, 6H), 5.58(d, 1H, J=9.9Hz), 4.50(m, 1H), 4.39(dd, 1H, J=8.4, 1.2Hz) 3.35(m,

1H), 3.22(m, 1H), 1.86-1.72(m, 2H), 1.61(m, 2H) 1.39(m, 2H), 0.992(t, 3H, J= 8.3, 3,9 Hz); ¹³C NMR(CDCl₃, 75MHz, ppm): δ= 195.8, 194.3, 133.1, 132.6, 130.2, 129.8, 128.0, 103.1, 63.5, 61.6, 38.4, 30.9, 28.3, 14.9, 14.0.

2-[6-(1-Benzoyl-2-oxo-2-phenyl-ethyl)-tetrahydro-pyran-2-yl]-1,3-diphenyl-propane-1,3-dione.

IR(KBr plate): 2931, 2344, 1696, 1559, 1450, 1273, 1192, 762cm⁻¹; ¹H NMR(CDCl₃, 300MHz, ppm): δ= 7.89(m, 4H), 7.66(m, 4H), 7.49-7.28(m, 12 H), 5.27(d, 2H, J=9Hz), 4.52(m, 2H), 1.82(m, 3H), 1.36(m, 3H); ¹³C NMR(CDCl₃, 75MHz, ppm): δ= 195.2, 189.2, 133.7, 133.3, 129.1, 128.6, 79.2, 74.2, 63.9, 33.1, 30.1, 29.0, 27.0, 23.1; MS(EI): m/z(%) 306, 223, 146, 105(100), 77; MS(ESI): m/z (%) 530(M⁺), 307; HRMS calc'd for C₂₀H₁₈O₃(M⁺-dibenzoylmethane): 306.12559; found, 306.12531.

1,3-Diphenyl-2-(tetrahydro-furan-2-yl)-propane-1,3-dione.

IR(KBr plate): 2943, 2319, 1691, 1603, 1442, 1289, 1072, 818, 685cm⁻¹; ¹H-NMR(CDCl₃, 300MHz, ppm): δ= 8.02(m, 4H), 7.53-7.41(m, 6H), 5.42(d, 1H, J=8.1Hz), 4.83(m, 1H), 3.83-3.69(m, 2H), 2.29(m, 2H), 1.95(m, 2H); ¹³C NMR(CDCl₃, 75MHz, ppm): δ= 194.7, 194.3, 137.0, 130.6, 138.8, 133.6, 129.0, 79.7, 68.4, 63.0, 30.8, 25.9; MS(EI) m/z(%): 224, 189, 105(100), 77; MS(ESI): m/z (%) 294.1 (M⁺) ; HRMS calc'd for C₁₂H₁₃O₂(M⁺-COPh) : 189.09155; found: 189.09171.

2-Cyclooct-2-enyl-1-phenyl-butane-1,3-dione.

One of the diastereoisomer can be partially isolated using crystallization. IR(KBr plate): 2923, 2855, 2360, 1708, 1660, 1447, 1354, 970cm⁻¹; ¹H NMR(CDCl₃, 300MHz, ppm): δ= 8.00-7.97(m, 2H), 7.57-7.43(m, 3H), 5.63(m, 1H), 5.17(m, 1H), 4.58(d, 1H, J=9.1Hz), 3.61(m, 1H), 2.40(m, 2H), 2.21(s, 3H), 2.11(m, 2H), 1.74(m, 2H), 1.49(m, 4H); ¹³C NMR(CDCl₃, 75MHz, ppm): δ= 204.4, 195.6, 133.8, 132.1, 130.4, 129.0, 70.3, 37.5, 33.8, 29.8, 28.1, 27.3, 25.6; MS(EI): m/z(%) 270(M⁺), 227(100), 165, 105, 77; HRMS calc'd for C₁₈H₂₂O₂: 270.1620; found, 270.1616.

Another diastereoisomer (from the mixture and some peaks are difficult to distinguished): ^1H NMR(CDCl_3 , 300MHz, ppm): δ = 4.41(d, 1H, J =8.6Hz), 3.46(m, 1H), 2.10(s, 3H); ^{13}C NMR(CDCl_3 , 75MHz, ppm): δ = 203.6, 194.0, 135.4, 69.6, 36.8, 34.3, 26.8, 24.5.

1-Phenyl-2-(tetrahydro-pyran-2-yl)-butane-1,3-dione.

one of the diastereoisomer can be partially isolated using a mixture of 5:1:1(hexanes, ethyl acetate, ether) on an analytical TLC. IR(KBr plate): 2936, 2348, 1708, 1656, 1555, 1450, 1233, 976 cm^{-1} ; ^1H NMR(CDCl_3 , 300MHz, ppm): δ = 8.03(m, 2H), 7.59-7.45(m, 3H), 4.64(d, 1H, J = 9.6Hz), 4.28(m, 1H), 4.01(m, 1H), 3.49(m, 1H), 2.24(s, 3H), 1.82(m, 1H), 1.59(m, 5H). ^{13}C NMR(CDCl_3 , 75MHz, ppm): 202.8, 193.8, 150.0, 136.9, 134.1, 133.9, 129.1, 70.3, 59.8, 30.5, 27.9, 26.1, 23.5; MS(EI): m/z (%) 203, 147, 105(100), 77; MS(ESI): m/z (%) 246.1 (M^+); HRMS calc'd for $\text{C}_{13}\text{H}_{15}\text{O}_2(\text{M}^+-\text{Ac})$: 203.10720; found: 203.10752. Another diastereoisomer (from the mixture and some peaks are difficult to distinguished): ^1H NMR(CDCl_3 , 300MHz, ppm): 4.69(d, 1H, J =9.6Hz), 3.82(m, 1H), 2.18(s, 3H); ^{13}C NMR(CDCl_3 , 75MHz, ppm): 203.1, 192.2, 148.8, 69.1, 60.4, 31.4, 28.5, 24.0.

Table 1. Crystal data and structure refinement for **1**.

Identification code	1
Empirical formula	C11.50 H11 O
Formula weight	165.20
Temperature	571(2) K
Wavelength	0.71073 Å
Crystal system, space group	orthorhombic, Pmn21
Unit cell dimensions	a = 17.307(14) Å alpha = 90 deg. b = 5.500(5) Å beta = 90 deg. c = 9.735(8) Å gamma = 90 deg.
Volume	926.6(13) Å ³
Z, Calculated density	4, 1.184 Mg/m ³
Absorption coefficient	0.074 mm ⁻¹
F(000)	352
Crystal size	.4 x .2 x .2 mm
Theta range for data collection	3.70 to 26.69 deg.
Limiting indices	-21 ≤ h ≤ 21, -6 ≤ k ≤ 6, -6 ≤ l ≤ 12
Reflections collected / unique	4302 / 1348 [R(int) = 0.1328]
Completeness to theta = 26.69	94.9 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	1348 / 1 / 138
Goodness-of-fit on F ²	1.013
Final R indices [I > 2sigma(I)]	R1 = 0.0722, wR2 = 0.2040
R indices(all data)	R1 = 0.0959, wR2 = 0.2295
Absolute structure parameter	-1(5)
Largest diff. peak and hole	0.255 and -0.290 e.Å ⁻³

Table 2. Atomic coordinates($\times 10^4$) and equivalent isotropic displacement parameters($\text{\AA}^2 \times 10^3$) for **1**.
 $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
O(1)	1045(6)	-712(15)	925(8)	119(3)
C(1)	865(6)	1189(18)	402(10)	72(2)
C(2)	0	2376(9)	849(6)	76(2)
C(3)	0	2299(7)	2399(5)	61(1)
C(4)	1265(3)	2209(8)	-659(5)	86(1)
C(5)	1949(5)	1008(14)	-965(8)	136(3)
C(6)	2453(4)	1914(18)	-1901(9)	131(2)
C(7)	2309(3)	3937(15)	-2579(8)	126(2)
C(8)	1635(3)	5235(9)	-2300(7)	109(2)
C(9)	1129(3)	4317(9)	-1345(5)	87(1)
C(10)	706(2)	3467(8)	2984(6)	88(1)
C(11)	927(3)	3071(11)	4335(6)	106(2)
C(12)	754(3)	778(10)	5059(6)	99(2)
C(13)	0	697(14)	5884(8)	98(2)
C(1A)	502(7)	940(20)	187(14)	57(3)
O(1A)	528(7)	-1248(12)	383(14)	113(4)

Table 3. Bond lengths [Å] and angles [deg] for 1.

O(1)-C(1)	1.204(11)
C(1)-C(4)	1.364(12)
C(1)-C(2)	1.690(10)
C(2)-C(3)	1.509(8)
C(2)-C(1)#1	1.690(10)
C(3)-C(10)	1.493(5)
C(3)-C(10)#1	1.493(5)
C(4)-C(9)	1.358(7)
C(4)-C(5)	1.388(9)
C(5)-C(6)	1.357(11)
C(6)-C(7)	1.317(9)
C(7)-C(8)	1.395(9)
C(8)-C(9)	1.373(8)
C(10)-C(11)	1.387(8)
C(11)-C(12)	1.476(8)
C(12)-C(13)	1.533(7)
C(13)-C(12)#1	1.533(7)
C(1A)-O(1A)	1.222(14)
C(1A)-C(1A)#1	1.74(2)
O(1A)-O(1A)#1	1.83(2)
O(1)-C(1)-C(4)	123.1(8)
O(1)-C(1)-C(2)	117.1(9)
C(4)-C(1)-C(2)	119.1(6)
C(3)-C(2)-C(1)#1	104.3(4)
C(3)-C(2)-C(1)	104.3(4)
C(1)#1-C(2)-C(1)	124.7(8)
C(10)-C(3)-C(10)#1	109.8(5)
C(10)-C(3)-C(2)	111.7(3)
C(10)#1-C(3)-C(2)	111.7(3)
C(9)-C(4)-C(1)	129.4(5)
C(9)-C(4)-C(5)	116.6(6)
C(1)-C(4)-C(5)	113.6(6)
C(6)-C(5)-C(4)	121.2(7)
C(7)-C(6)-C(5)	121.7(6)
C(6)-C(7)-C(8)	119.6(6)
C(9)-C(8)-C(7)	118.5(5)
C(4)-C(9)-C(8)	122.5(5)
C(11)-C(10)-C(3)	121.3(4)
C(10)-C(11)-C(12)	122.1(5)
C(11)-C(12)-C(13)	116.6(5)
C(12)-C(13)-C(12)#1	116.6(6)
O(1A)-C(1A)-C(1A)#1	92.1(7)
C(1A)-O(1A)-O(1A)#1	87.9(7)

Symmetry transformations used to generate equivalent atoms:
#1 -x,y,z

Table 4. Anisotropic displacement parameters($\text{\AA}^2 \times 10^3$) for **1**.
The anisotropic displacement factor exponent takes the form:
 $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
O(1)	154(6)	100(5)	103(5)	28(4)	30(5)	66(5)
C(1)	77(6)	77(5)	62(5)	-2(4)	-4(5)	25(5)
C(2)	120(4)	48(2)	62(3)	0(2)	0	0
C(3)	66(3)	53(2)	66(3)	2(2)	0	0
C(4)	112(3)	87(3)	59(2)	-7(2)	0(2)	14(2)
C(5)	165(6)	148(5)	95(4)	-13(4)	4(4)	60(4)
C(6)	95(4)	187(7)	110(5)	-26(5)	-7(4)	18(4)
C(7)	74(3)	188(6)	116(5)	-11(5)	-7(3)	-37(3)
C(8)	100(3)	120(3)	107(4)	23(3)	-8(3)	-31(3)
C(9)	77(2)	97(3)	87(3)	8(2)	-7(2)	-7(2)
C(10)	79(2)	96(3)	87(3)	21(2)	-13(2)	-21(2)
C(11)	98(3)	127(4)	92(3)	24(3)	-33(3)	-41(3)
C(12)	83(3)	124(3)	89(3)	26(3)	-21(2)	1(3)
C(13)	114(5)	105(4)	75(4)	16(3)	0	0
C(1A)	54(7)	60(5)	57(7)	-11(4)	8(6)	0(5)
O(1A)	141(8)	43(3)	156(10)	-8(5)	64(8)	11(4)

Table 5. Hydrogen coordinates($\times 10^4$) and isotropic displacement parameters($\text{\AA}^2 \times 10^3$) for **1**.

	x	y	z	U(eq)
H(2A)	0	4089	573	150(40)
H(3A)	0	588	2681	74
H(5A)	2064	-444	-520	163
H(6A)	2912	1087	-2069	157
H(7A)	2655	4497	-3238	151
H(8A)	1529	6688	-2752	131
H(9A)	677	5169	-1160	104
H(10A)	1003	4481	2431	105
H(11A)	1192	4290	4799	127
H(12A)	1178	433	5680	118
H(12B)	739	-521	4385	118
H(13A)	0	2058	6518	118
H(13B)	0	-778	6430	118

Another diastereoisomer

Another diastereoisomer