A New Route to Cyclopentenones via Ruthenium-Catalyzed Carbonylative Cyclization of Allylic Carbonates with Alkenes

Yasuhiro Morisaki, Teruyuki Kondo,* and Take-aki Mitsudo*

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering,
Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

mitsudo@scl.kyoto-u.ac.jp

Supporting Information

Experimental details, and characterization of all new compounds pp 1-6

General. GLC analyses were carried out on a gas chromatograph equipped with a glass column (3 mm i.d. x 3 m) packed with Silicone SE-30 (5% on Chromosorb W(AW-DMCS), 80-100 mesh). The products were isolated by Kugelrohr distillation, and purified on a recycling preparative HPLC (Japan Analytical Industry Co. Ltd., Model 908) equipped with JAIGEL-1H and 2H columns (GPC) using $CHCl_3$ as an eluent. The ^{1}H-NMR spectra were recorded at 300 and/or 400 MHz. ^{13}C-NMR spectra were recorded at 75 and/or 100 MHz. Samples were analyzed in $CDCl_3$, and the chemical shift values are expressed relative to Me_4Si as an internal standard. IR spectra were obtained on a Nicolet Impact 410 spectrometer. Elemental analyses were performed at the Microanalytical Center of Kyoto University.

Materials. The reagents used in this study were dried and purified before use by standard procedures. Carbon monoxide (>99.9%) was used without purification. Allylic carbonates (**1a-h**) were prepared from the corresponding alcohols and methyl chloroformate according to the reported procedure.[1,2] The norbornene derivatives, **2b**[3] and **2c**,[4] were prepared by the method in the literature. $[RuCl_2(CO)_3]_2$ and $Ru_3(CO)_{12}$ were obtained commercially and used without further purification. [(*p*-cymene)$RuCl_2]_2$,[5] Cp*RuCl(cod),[6] $RuCl_2(PPh_3)_3$,[7] $Ru(CO)_3(PPh_3)_2$,[8] and (η^3-C_3H_5)$RuBr(CO)_3$ (**5**)[9] were prepared as described in the literature.

Carbonylative Cyclization of Allylic Carbonates (1a-g) with 2-Norbornene Derivatives (2a-2c). A mixture of allylic carbonate (1.0 mmol), 2-norbornene derivative (2.0 mmol), $[RuCl_2(CO)_3]_2$ (12.8 mg, 0.025 mmol) or (η^3-C_3H_5)$RuBr(CO)_3$ (**5**) (15.3 mg, 0.050 mmol), Et_3N (10.1 mg, 0.10 mmol), and THF (2.0-8.0 mL) was placed in a 50-mL stainless steel autoclave under a flow of argon. Carbon monoxide was then pressurized to 3 atm at room temperature, and the mixture was magnetically stirred at 120-150 °C for 5-12 h. After cooling, the products were isolated by Kugelrohr distillation, and purified by recycling preparative HPLC.

Carbonylative Cyclization of Cinnamyl Methyl Carbonate (1f) and Methyl 1-Phenylallyl Carbonate (1g) with 2-Norbornene (2a). A mixture of carbonate (**1f** or **1g**) (1.0 mmol), 2-norbornene (**2a**) (103 mg, 1.1 mmol),

$[RuCl_2(CO)_3]_2$ (10.2 mg, 0.020 mmol), Et_3N (6.0 mg, 0.060 mmol), and THF (2.0 mL) was placed in a 50-mL stainless steel autoclave under a flow of argon. Carbon monoxide was then pressurized to 3 atm at room temperature, and the mixture was magnetically stirred at 120 °C for 3 h. After cooling, the products were isolated by Kugelrohr distillation, and purified by recycling preparative HPLC.

Stoichiometric Reaction of (η^3-C_3H_5)RuBr$(CO)_3$ (5) with 2-Norbornene (2a). A mixture of (η^3-C_3H_5)RuBr$(CO)_3$ (**5**) (30.6 mg, 0.10 mmol), 2-norbornene (**2a**) (18.8 mg, 0.20 mmol), and THF (2.0 mL) was placed in a 50-mL stainless steel autoclave under a flow of argon. Carbon monoxide was then pressurized to 3 atm at room temperature, and the mixture was magnetically stirred at 120 °C for 12 h. After cooling, the product was isolated by Kugelrohr distillation.

Intramolecular Carbonylative Cyclization of Methyl 5,5-dicarbomethoxy-7-methyl-2,7-octadienyl Carbonate (1h). A mixture of 5,5-dicarbomethoxy-7-methyl-2,7-octadienyl methyl carbonate (**1h**) (314 mg, 1.0 mmol), $[RuCl_2(CO)_3]_2$ (12.8 mg, 0.025 mmol), Et_3N (10.1 mg, 0.10 mmol), and THF (5.0 mL) was placed in a 50-mL stainless steel autoclave under a flow of argon. Carbon monoxide was then pressurized to 3 atm at room temperature, and the mixture was magnetically stirred at 120 °C for 12 h. After cooling, the products were isolated by Kugelrohr distillation, and purified by recycling preparative HPLC.

Compounds **2b**,[2] **3a**,[10] **3b**,[11] **3d**,[10] **3e**,[12] **3f**,[13] and **4a**[10] have already been reported. All of the new compounds are characterized below.

5,5-Dicarbomethoxy-7-methyl-2,7-octadienyl methyl carbonate (1h). Colorless oil, bp 120 °C (1.0 mmHg, Kugelrohr); IR (neat): 1740 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 1.58 (s, 3H), 2.59 (d, 2H, $J = 6.06$ Hz), 2.62 (s, 2H), 3.64 (s, 6H), 3.70 (s, 3H), 4.47 (d, 2H, $J = 5.14$ Hz), 4.69 (s, 1H), 4.81 (s, 1H), 5.55-5.67 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 22.9, 35.4, 40.4, 52.3, 54.6, 57.1, 67.8, 115.8, 127.7, 130.5, 140.1, 155.4, 171.2; Mass (EI) m/z 314 (M^+). Anal. Calcd for $C_{15}H_{22}O_7$: C 57.32; H 7.05. Found: C 57.45; H 7.30.

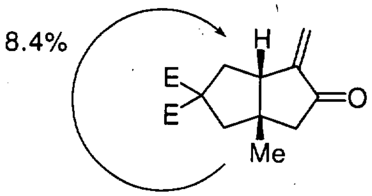
Diethyl *exo*-tricyclo[4.2.1.$0^{2,5}$]nona-3,7-diene-3,4-dicarboxylate (2c). Pale yellow oil, bp 110-115 °C (1.0 mmHg, Kugelrohr); IR (neat): 1721 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.25-1.38 (m, 2H), 1.29 (t, 6H, *J* = 7.08 Hz), 2.52 (s, 2H), 2.67 (s, 2H), 4.21 (q, 4H, *J* = 7.08 Hz), 6.14 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.1, 38.2, 39.5, 44.1, 60.7, 135.9, 144.9, 161.5; Mass (EI) m/z 262 (M^+). Anal. Calcd for $C_{15}H_{18}O_4$: C 68.68; H 6.92. Found: C 68.81; H 7.01.

Diethyl *exo,exo*-4-methyltetracyclo[5.4.1.$0^{2,6}$.$0^{8,11}$]dodeca-4,9-dien-3-one-9,10-dicarboxylate (3c). Pale yellow oil, bp 160-170 °C (1.0 mmHg, Kugelrohr); IR (neat): 1731, 1705 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.86 (d, 1H, *J* = 11.72 Hz), 1.12 (d, 1H, *J* = 11.72 Hz), 1.24 (t, 3H, *J* = 7.08 Hz), 1.25 (t, 3H, *J* = 7.08 Hz), 1.71 (s, 3H), 2.11 (d, 1H, *J* = 4.89 Hz), 2.19 (s, 1H), 2.43 (s, 1H), 2.53 (br, 1H), 2.76 (s, 1H), 2.78 (s, 1H), 4.15 (q, 2H, *J* = 7.08 Hz), 4.16 (q, 2H, *J* = 7.08 Hz), 7.09 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 10.0, 14.0, 14.1, 23.7, 35.9, 36.1, 46.6, 46.7, 47.2, 51.9, 60.8, 60.9, 142.2 (two overlapping signals), 145.0, 158.5, 160.7, 161.0, 209.9; Mass (EI) m/z 330 (M^+). Anal. Calcd for $C_{19}H_{22}O_5$: C 69.07; H 6.71. Found: C 68.98; H 6.98.

4-Benzylidenetricyclo[5.2.1.$0^{2,6}$]decan-3-one (6a). White solid, mp 99.0-100.3 °C; IR (KBr): 1696 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.07 (d, 1H, *J* = 10.28 Hz), 1.14 (d, 1H, *J* = 10.28 Hz), 1.17-1.34 (m, 2H), 1.50-1.59 (m, 2H), 2.21 (s, 1H), 2.33 (s, 1H), 2.34 (s, 1H), 2.53-2.61 (m, 2H), 3.17-3.28 (m, 1H), 7.29 (s, 1H), 7.34-7.55 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 28.4, 28.7, 33.6, 34.8, 40.4, 42.4, 44.4, 56.0, 128.4, 129.2, 130.8, 132.1, 135.6, 137.2, 211.2; Mass (EI) m/z 238 (M^+). Anal. Calcd for $C_{17}H_{18}O$: C 85.67; H 7.61. Found: C 85.40; H 7.68.

X-ray Structural Determination of 6a. A single crystal of **6a** was mounted and placed on a Rigaku AFC-7R diffractometer. The unit cell was determined by the automatic indexing of 20 centered reflections and confirmed by examination of axial photographs. Intensity data were collected using graphite monochromated Mo Kα X-radiation (λ = 0.71069 Å). Check reflections were measured every 150 reflections; the data were scaled accordingly and corrected for Lorentz, polarization, and absorption effects. The structure was determined using Patterson and standard difference map techniques on an O2 computer using SIR92.[14] Systematic absences were uniquely consistent with the space group $P2_12_12_1$ [No. 19].

Dimethyl 4-vinylidene-3-oxobicyclo[3.3.0^{1,5}]octane-7,7-dicarboxylate (6b). Colorless oil, bp 130-135 °C (1.0 mmHg, Kugelrohr); IR (neat): 1731 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.12 (s, 3H), 2.21 (d, 1H, J = 18.55 Hz), 2.22 (dd, 1H, J = 6.84, 13.67 Hz), 2.25 (d, 1H, J = 14.16 Hz), 2.36 (d, 1H, J = 14.16 Hz), 2.44 (d, 1H, J = 18.55 Hz), 2.77 (dd, 1H, J = 7.81, 13.67 Hz), 2.85 (dd, 1H, J = 6.84, 7.81 Hz), 3.60 (s, 3H), 3.69 (s, 3H), 5.26 (d, 1H, J = 2.20 Hz), 5.98 (d, 1H, J = 2.20 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 27.5, 40.4, 44.8, 46.7, 51.4, 52.8, 52.9, 53.0, 61.1, 119.2, 147.9, 172.4, 172.5, 205.9; Mass (EI) m/z 266 (M^+). Anal. Calcd for $C_{14}H_{18}O_5$: C 63.15; H 6.81. Found: C 63.44; H 7.08. Irradiation of the methyl protons at δ 1.12 gave a 8.4% NOE of the C-5 hydrogen at δ 2.85. The stereochemistry of the major isomer was therefore assigned as shown:



6 b

References

(1) Tsuji, J.; Sato, K.; Okumoto, H. *J. Org. Chem.* **1984**, *49*, 1341.

(2) Terakado, T.; Murai, K.; Miyazawa, M.; Yamamoto, K. *Tetrahedron* **1994**, *50*, 5705.

(3) Kaupp, G.; Prinzbach, H. *Chem. Ber.* **1971**, *104*, 182.

(4) Mitsudo, T.; Naruse, H.; Kondo, T.; Ozaki, T.; Watanabe, Y. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 581.

(5) Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233.

(6) Oshima, N.; Suzuki, H.; Moro-oka, Y. *Chem. Lett.* **1984**, 1161.

(7) Hallman, P. S.; Stephenson, T. A.; Wilkinson, G. *Inorg. Synth.* **1970**, *12*, 237.

(8) Wonchoba, E. R.; Parshall, G. W. *Inorg. Synth.* **1974**, *15*, 50.

(9) Sbrana, G.; Braca, g.; Piacenti, F.; Pino, P. *J. Organomet. Chem.* **1968**, *13*, 240.

(10) Larock, R. C.; Takagi, K.; Burkhart, J. P.; Herchberger, S. S. *Tetrahedron* **1986**, *42*, 3759.

(11) Khand, I. U.; Knox, G. R.; Pauson, P. L.; Watts, W. E.; Foreman, M. I. *J. Chem. Soc., Perkin Trans. 1* **1973**, 977.

(12) Derdau, V.; Laschat, S.; Jones, P. G. *Heterocycles* **1998**, *48*, 1445.

(13) Montenegro, E.; Moyano, A.; Pericas, M. A.; Riera, A.; Alvarez-Larena, A.; Piniella, J.-F. *Tetrahedron: Asymmetry* **1999**, 10, 457.

(14) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A.; Polidori, G. *J. Appl. Cryst.* **1994**, *27*, 435.