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Spectral Data for "Synthesis of Cyclopropanes via Organoiron Methodology: Stereoselective Preparation of Bi(cyclopropyl)s"

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Synthesis of Cyclopropanes via Organoiron Methodology:
Stereoselective Preparation of Biscyclopropanes
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Dichlorocyclopropanation of 4a (6/7): To a solution of 4a (1.83 g, 6.27 mmol) and cetyltrimethylammonium bromide (27.6 mg, 0.076 mmol) in CHCl₃ (40 mL) was added 50% aqueous NaOH. The biphasic mixture was vigorously stirred at room temperature for 80 h. After this time, the mixture was diluted with water (50 mL), extracted several times with CH₂Cl₂, and the combined extracts were dried (MgSO₄) and concentrated under reduced pressure. Analysis of the crude product by ¹H NMR spectroscopy indicated this to be a mixture of 6, 7 and unreacted 4a (ca. 6 : 3 : 2 by integration). Purification of the residue by column chromatography (SiO₂, hexanes–ethyl acetate = 96.5:3.5) gave a mixture of 7 and 4a as an orange solid, followed by 6 as a yellow solid (863 mg, 2.30 mmol, 37%). Recrystallization of the mixture of 7 and 4a gave crystals of 7 which were suitable for X-ray diffraction analysis.

6: mp 66-68 °C; ¹H NMR (300 MHz, CDCl₃) δ 0.26 (d, J = 6.0 Hz, 1H), 1.08-1.21 (m, 2H), 1.47 (dd, J = 5.4, 7.5 Hz, 1H), 2.49 (dd, J = 1.9, 9.1 Hz, 1H), 3.03 (q, J = 6.0 Hz, 1H), 3.60 (br d, J = 6.6 Hz, 1H), 3.67 (s, 3H), 4.36 (br t, J = 5.7 Hz, 1H), 4.62 (ddd, J = 5.7, 6.6, 9.6 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 13.0, 26.4, 38.6, 39.8, 51.6, 54.2, 61.5, 97.9, 180.0, 203.9, 210.1, 210.6.

7: mp 130-132 °C; ¹H NMR (300 MHz, CDCl₃) δ 0.18 (d, J = 9.0 Hz, 1H), 1.06 (t, J = 7.2 Hz, 1H), 1.18 (dt, J = 7.5, 10.2 Hz, 1H), 1.37 (dd, J = 6.3, 9.9 Hz, 1H), 2.50-2.61 (m, 1H), 2.89-2.99 (m, 1H), 3.65-3.72 (m & s, 4H total), 4.65-4.75 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 11.4,
(1S*,2R*,3R*,4R*)-5,5-Dichloro-1-methoxycarbonyl-2-vinylbicyclopropane (rac-11): To a solution of 6 (400 mg, 1.07 mmol) in methanol (13 mL) at room temperature was added portion-wise ceric ammonium nitrate (4.1 g, 7.5 mmol) over a period of 10 min. The mixture was stirred for an additional 10 min and then poured into brine and extracted several times with ethyl acetate. The combined organic extracts were washed with water, followed by saturated aqueous NaHCO₃ and brine, dried (MgSO₄) and concentrated under reduced pressure to give 11 as a colorless syrup (250 mg, 1.06 mmol, 99%). 11: ¹H NMR (300 MHz, CDCl₃) δ 1.28-1.42 (m, 2H), 1.52 (td, J = 4.5, 8.1 Hz, 1H), 1.70 (dd, J = 6.1, 9.4 Hz, 1H), 1.90 (t, J = 4.8 Hz, 1H), 2.26 (br dt, J = 4.8, 8.1 Hz, 1H), 3.74 (s, 3H), 5.19 (br d, J = 10.2 Hz, 1H), 5.29 (br d, J = 17.1 Hz, 1H), 5.63 (ddd, J = 8.1, 10.2, 17.1 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 27.3, 27.5, 28.3, 29.0, 29.8, 52.2, 60.7, 118.4, 133.6, 173.0. Anal. Calcd for C₁₀H₁₂O₂Cl₂·0.3H₂O: C, 49.94; H, 5.28. Found: C, 49.90; H, 5.16.

Simmons-Smith cyclopropanation of 4c (8/9): To a solution of 4c (4.31 g, 13.4 mmol) in anhydrous CH₂Cl₂ at -20 °C was added dropwise a solution of diethylzinc in hexanes (68.4 mL, 1.0 M, 68.4 mmol) followed by diiodomethane (5.4 mL, 67 mmol). The reaction mixture was allowed to gradually warm to room temperature over a 3 h period and the mixture was stirred for an additional 1 h. Saturated aqueous NH₄Cl (70 mL) was added and mixture was diluted with ether (400 mL) and 10% aqueous HCl (70 mL). The layers were separated and the organic layer was washed with saturated aqueous Na₂SO₃ (70 mL), followed by saturated aqueous NaHCO₃ (70 mL), brine, dried (MgSO₄) and concentrated under reduced pressure. Analysis of the crude product by ¹H NMR spectroscopy indicated this to be a mixture of 8 and 9 (4.5 : 1 by...
integration). Purification of the residue by column chromatography (SiO_{2}, hexanes–ethyl acetate = 6.5:3.5) gave 9 as an orange oil followed by 8 as a red color syrup (3.15 g, 9.37 mmol, 70%).

9: IR (CH_{2}Cl_{2}) 3447, 2062, 1698 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 0.18 (d, \(J = 8.7 \text{ Hz, } 1\text{H}\)), 0.21-0.35 (m, 2H), 0.38-0.46 (m, 1H), 0.80 (m, 1H), 1.70 (br s, OH), 2.40-2.55 (m, 2H), 3.29 (d, \(J = 6.3 \text{ Hz, } 2\text{H}\)), 3.60 (d, \(J = 7.2 \text{ Hz, } 1\text{H}\)), 3.67 (s, 3H), 4.40-4.65 (m, 2H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 9.2, 13.9, 19.2, 26.0, 43.0, 51.6, 54.5, 65.8, 66.4, 97.9, 181.0, 204.1, 210.7, 211.0. FAB-HRMS m/z 337.0363 (calcd for C\(_{14}\)H\(_{17}\)O\(_6\)Fe (M+H\(^{+}\)) m/z 337.0375).

8: IR (CH\(_2\)Cl\(_2\)) 3447, 2067, 2002, 1698 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 0.18 (d, \(J = 9.0 \text{ Hz, } 1\text{H}\)), 0.19-0.30 (m, 3H), 0.90-1.00 (m, 1H), 1.60 (br s, OH), 2.49 (m & dd, \(J = 2.4, 11.4 \text{ Hz, } 2\text{H total}\)), 3.30 (dd, \(J = 7.2, 11.2 \text{ Hz, } 1\text{H}\)), 3.41 (dd, \(J = 6.6, 11.1 \text{ Hz, } 1\text{H}\)), 3.61 (d, \(J = 8.7 \text{ Hz, } 1\text{H}\)), 3.67 (s, 3H), 4.50 (t, \(J = 7.2 \text{ Hz, } 1\text{H}\)), 4.59 (td, \(J = 7.7, 11.4 \text{ Hz, } 1\text{H}\)); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 8.1, 14.0, 20.4, 26.2, 42.9, 51.6, 54.6, 65.8, 66.6, 97.9, 181.0, 204.0, 210.6. FAB-HRMS m/z 337.0380 (calcd for C\(_{14}\)H\(_{17}\)O\(_6\)Fe (M+H\(^{+}\)) m/z 337.0375).

(1S\(^*\),2R\(^*\),3R\(^*\),4S\(^*\),6R\(^*\))-6-Hydroxymethyl-1-methoxycarbonyl-2-vinylbicyclopropane (rac-12): To a solution of 8 (690 mg, 2.05 mmol) in methanol (24 mL) at room temperature was added portion-wise ceric ammonium nitrate (7.01 g, 12.8 mmol) over a period of 10 min. The mixture was stirred for an additional 20 min and then poured into brine (30 mL) and extracted with ethyl acetate (3 x 40 mL). The combined organic extracts were washed with water (3 x 30 mL), followed by saturated aqueous NaHCO\(_3\) (30 mL) and brine (30 mL), dried (MgSO\(_4\)) and concentrated under reduced pressure to give 12 as a colorless syrup (324 mg, 1.65 mmol, 80%).

12: IR (CH\(_2\)Cl\(_2\)) 1726 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 0.49-0.62 (m, 3H), 1.03-1.14 (m, 1H), 1.45 (td, \(J = 4.8, 9.3 \text{ Hz, } 1\text{H}\)), 1.61 (t, \(J = 4.5 \text{ Hz, } 1\text{H}\)), 2.18 (dt, \(J = 4.4, 9.0 \text{ Hz, } 1\text{H}\)), 3.40 (dd, \(J = 6.9, 11.1 \text{ Hz, } 1\text{H}\)), 3.50 (dd, \(J = 6.6, 11.4 \text{ Hz, } 1\text{H}\)), 3.67 (s, 3H), 5.15 (br d, \(J = 10.5 \text{ Hz, } 1\text{H}\)), 5.40 (dd, \(J = 9.6, 12.3 \text{ Hz, } 1\text{H}\)), 5.60 (s, 1H), 7.00-7.15 (m, 1H), 7.40 (d, \(J = 8.2 \text{ Hz, } 1\text{H}\)).
1H), 5.27 (br d, J = 17.4 Hz, 1H), 5.65 (ddd, J = 9.0, 10.2, 17.1 Hz, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 10.6, 14.8, 21.0, 27.0, 30.8, 31.5, 52.1, 66.6, 117.4, 134.7, 173.7. Anal. Caled for C$_{11}$H$_{16}$O$_3$: C, 67.32; H, 8.21. Found: C, 66.94; H, 8.22.
$^1$H NMR
(300 MHz, CDCl$_3$)

![NMR Spectrum](image)

**Data**

- **F1**: 399.751
- **F2**: 100.526
- **SW1**: 6410
- **QF1**: 2385.5
- **PTSId**: 13132
- **EX**: s2 pul
- **PW**: 7.7 us
- **PD**: 1.0 sec
- **NA**: 8
- **LB**: 0.0

**User**: -- **Date**: Apr 17 2007
$^{1}$H NMR
(300 MHz, CDCl$_3$)

STANDARD 1H OBSERVE

F1: 300.145  F2: 75.479  SW1: 4810  OF1: 1804.0
EX: s2pul  PW: 6.3 usec  PD: 1.0 sec  NA: 8  LB: 0.0

WinNuts - $srkp053-f2.fid$
$^{1}$H NMR
(300 MHz, CDCl$_3$)
$^{1}$H NMR
(300 MHz, CDCl$_3$)

HNMR (300 MHz, CDCl$_3$)

2.68, 8.00, 8.89, 6.71
\[^1\text{H NMR}\]

(300 MHz, CDCl\textsubscript{3})