

8-2-2006

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Published version. *Journal of Chemical Crystallography*, Volume 36, No. 11 (August, 2006):777-780.  
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# Crystal and molecular structure of bis(8-phenylmenthyl) 2-(2-methyl-5-oxo-3-cyclohexen-1-yl)propandioate, $C_{42}H_{54}O_5 \cdot CH_3CN$

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Received December 20, 2005; accepted July 13, 2006  
Published Online August 1, 2006

The X-ray crystal structure of the title compound, as crystallized from acetonitrile-water was determined. The relative stereochemistry of the cyclohexenone ring with respect to the 8-phenylmenthyl esters was determined. The title compound crystallizes in the noncentrosymmetric space group  $P2_1$ , with  $a = 8.9850(10)$  Å,  $b = 15.575(3)$  Å,  $c = 14.478(2)$  Å,  $\beta = 94.61(2)^\circ$ , and  $D_{\text{calc}} = 1.118$  g cm<sup>-3</sup> for  $Z = 2$ .

**KEY WORDS:** 2-cyclohexenone; 8-phenylmenthyl esters.

As part of our research program on the application of acyclic (pentadienyl)iron(1+) cations in synthesis,<sup>1</sup> we discovered that the reaction of (3-methylpentadienyl)Fe(CO)<sub>3</sub><sup>+</sup> (**1**) with sodium malonates, followed by work up with NaHCO<sub>3</sub>, gave 4,5-disubstituted cyclohexenones **2** (Scheme 1).<sup>2</sup> This reaction presumably occurs via nucleophilic attack at an internal dienyl carbon, on the face opposite to iron, to afford a (2-pentene-1,5-diyl)iron species **3** which undergoes CO insertion to afford the iron acyl complex **4**. Reductive elimination of **4** and subsequent conjugation of the double bond affords **2**. Since the cation **1** is planar symmetric, nucleophilic attack at either C2 or C4 would give enantiomeric prod-

ucts. Toward this end, reaction of **1** with the anion from bis[(-)-8-phenylmenthyl]malonate gave the cyclohexenone (-)-**2b** as a single diastereomer in excellent yield. In order to assign the stereochemistry at C4,C5 relative to the 8-phenylmenthyl esters, X-ray diffraction analysis of **2b** was undertaken.

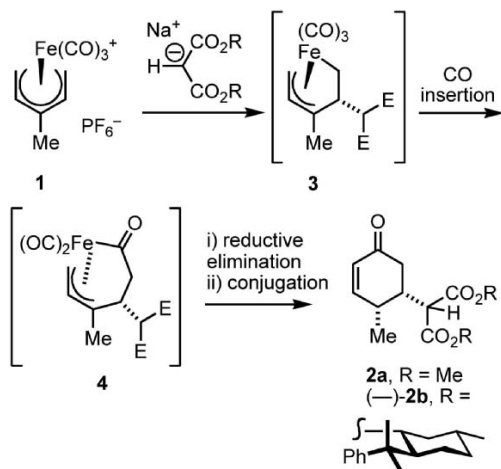
## Experimental section

Crystallization of **2b** from water-acetonitrile gave a sample which contained one molecule of acetonitrile per cyclohexenone. A crystal (0.23 × 0.24 × 0.35 mm) was attached to a glass fiber and mounted on a Bruker P4 diffractometer. The data were collected at 298 K using graphite monochromatized MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å) and the  $\Theta/2\Theta$  mode in the  $\Theta$  range 1.92–25.01°. No absorption correction was used. The structure was resolved by direct methods and the data were refined by full-matrix

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Scheme 1

least squares based on  $F^2$ .<sup>3</sup> A total of 4801 reflections were collected (3991 independent reflections,  $R_{\text{int}} = 0.0312$ ). The experimental crystallographic data is given in Table 1, and selected

**Table 1.** Crystal Data and Summary of Intensity Data Collection and Structure Refinement

Compound	$\text{C}_{44}\text{H}_{57}\text{NO}_5$
CCDC Deposit No.	284152
Color	Colorless
Crystal dimensions (mm)	$0.23 \times 0.24 \times 0.35$
Formula weight	679.91
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	
$a$ (Å)	8.9850(10)
$b$ (Å)	15.575(3)
$c$ (Å)	14.478(2)
$\beta$ (°)	94.61(2)
Cell volume (Å <sup>3</sup> )	2019.5(5)
$Z$	2
Density (calculated, $\text{g cm}^{-3}$ )	1.118
Absorption coefficient ( $\text{mm}^{-1}$ )	0.072
Diffractometer	Bruker P4
Radiation	Mo $K\alpha$ ( $\lambda = 0.71073$ Å)
$\theta$ range, deg	1.92–25.01
Reflections collected/unique	4801/3991 [ $R_{\text{int}} = 0.0312$ ]
Range of $h, k, l$	–10 to 1, –18 to 1, –17 to 17
Structure solution	Full-matrix least-squares on $F^2$
Absorption correction	none
Data/restraints/parameters	3991/1/451
Goodness-of-fit on $F^2$	0.965
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0565$ , $\omega R_2 = 0.1192$
$R$ indices (all data)	$R_1 = 0.1312$ , $\omega R_2 = 0.1473$
Largest feature ( $\text{eÅ}^{-3}$ )	0.291 and –0.138
Temperature (K)	293(2)

**Table 2.** Selected Bond Lengths (Å) and Bond Angles (°)

C(1)–C(7)	1.551(7)	C(21)–C(22)	1.327(8)
C(7)–C(8)	1.545(9)	C(22)–C(23)	1.482(8)
C(7)–C(9)	1.510(7)	C(23)–C(45)	1.518(9)
C(7)–C(10)	1.582(7)	C(25)–C(26)	1.510(7)
C(10)–C(11)	1.520(7)	C(26)–O(2)	1.189(7)
C(10)–C(15)	1.514(8)	C(26)–O(4)	1.344(6)
C(11)–C(12)	1.510(8)	C(27)–C(28)	1.532(7)
C(12)–C(13)	1.534(8)	C(27)–C(32)	1.512(6)
C(13)–C(14)	1.515(7)	C(27)–O(4)	1.478(5)
C(13)–C(16)	1.513(7)	C(28)–C(35)	1.559(7)
C(14)–C(15)	1.503(7)	C(29)–C(28)	1.544(7)
C(15)–O(1)	1.467(5)	C(29)–C(30)	1.521(6)
C(17)–C(25)	1.530(7)	C(30)–C(31)	1.499(7)
C(17)–O(1)	1.321(6)	C(31)–C(32)	1.531(7)
C(17)–O(3)	1.201(6)	C(31)–C(33)	1.530(7)
C(18)–C(19)	1.508(6)	C(35)–C(36)	1.549(9)
C(18)–C(23)	1.524(6)	C(35)–C(37)	1.540(10)
C(18)–C(25)	1.546(6)	C(35)–C(38)	1.538(8)
C(19)–C(20)	1.506(7)	C(60)–C(61)	1.409(12)
C(20)–C(21)	1.443(8)	C(61)–N(1)	1.093(13)
C(20)–O(5)	1.213(6)		
C(18)–C(19)–C(20)	112.9(4)	C(19)–C(18)–C(25)	114.0(4)
C(19)–C(20)–C(21)	117.6(5)	C(23)–C(18)–C(25)	111.7(4)
C(20)–C(21)–C(22)	122.0(6)	C(18)–C(23)–C(45)	114.5(5)
C(21)–C(22)–C(23)	123.4(6)	C(22)–C(23)–C(45)	109.8(5)
C(18)–C(23)–C(22)	111.0(5)	C(17)–C(25)–C(18)	111.2(4)
C(19)–C(18)–C(23)	111.2(4)	C(17)–C(25)–C(26)	106.1(4)
C(19)–C(20)–O(5)	120.9(5)	C(18)–C(25)–C(26)	111.1(4)
C(21)–C(20)–O(5)	121.5(5)		

bond lengths and angles are given in Table 2. The bond distances within the aromatic rings ranged from 1.336(8) to 1.396(9) Å [average = 1.373 Å].

## Results and discussion

A drawing of the molecule and the crystallographic numbering is given in Fig. 1. This reveals the *cis*-disubstituted relative stereochemistry about the cyclohexenone ring. Furthermore, on the basis of the known configuration of the (–)-8-phenylmenthyl group, the absolute configurations at C18 and C23 were found to be *S* and *S* respectively. To our knowledge, there are no crystal structures of a 4,5-disubstituted-2-cyclohexenone. However, the bond distances and angles within the cyclohexenone ring of **2b** (Table 2) are within the average values found for other substituted cyclohexenones.<sup>4</sup>

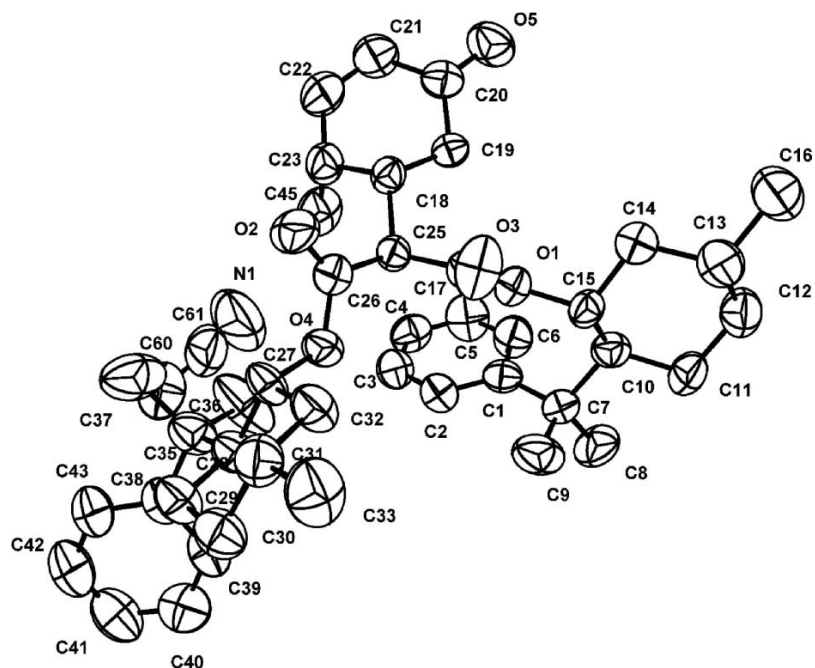


Fig. 1. ORTEP view of **2b** with crystallographic numbering scheme (50% probability ellipsoids).

Esters of 8-phenylmenthol have found use in diastereoselective transformations at either the  $\alpha$  or  $\beta$  carbon.<sup>5</sup> The rationale for this selectivity relies blocking of one face of the ester by the phenyl group (see A, Fig. 2). This orientation of the 1-methyl-1-phenylethyl group with respect

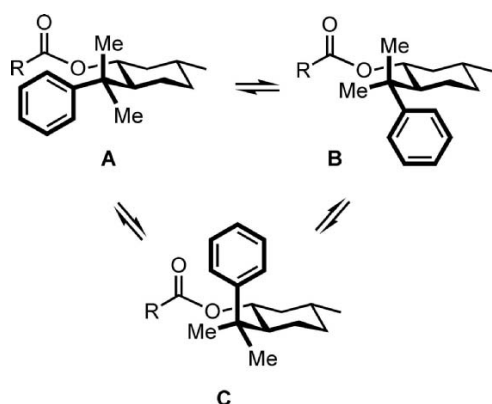


Fig. 2. Conformational possibilities for the side chain of 8-phenylmenthyl esters.

to the cyclohexane ring is observed in a number of crystal structures of (–)-8-phenylmenthyl esters.<sup>6</sup> Diastereoselective alkylation of bis[(–)-8-phenylmenthyl]malonates has been utilized for the enantioselective preparation of 2-vinyl-1,1-cyclopropanedicarboxylates and 2-iodomethyl-1,1-cyclopropanedicarboxylates, as well as for diastereoselective addition to pyridinium cations.<sup>7</sup> The present structure for **2b** is the first for any bis[(–)-8-phenylmenthyl]malonate. Notably, the side chain of the *pro-R* ester group adopts conformer A, while the side chain of the *pro-S* ester group adopts a conformer similar to B (Fig. 2). Only a few crystal structures of 8-phenylmenthyl esters exhibit conformer B,<sup>8</sup> while none of the crystal structures exhibit conformer C.

**Supplementary material** Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as CCDC-284152. These data can be obtained free of charge from CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: (44(0) 1223-336033; email: deposit@ccdc.cam.ac.uk.

## Acknowledgment

This material is based upon work supported by the National Science Foundation (CHE-0415771).

## References

- (a) Li, S.; Donaldson, W.A. *Synthesis* **2003**, 2064. (b) Yun, Y.K.; Godula, K.; Cao, Y.; Donaldson, W.A. *J. Org. Chem.* **2003**, *68*, 901. (c) Lukesh, J.M.; Donaldson, W.A. *Chem. Commun.* **2005**, 110. (d) Wallock, N.J.; Donaldson, W.A. *Org. Lett.* **2005**, *7*, 2047.
- Chaudhury, S.; Donaldson, W.A. *J. Am. Chem. Soc.* **2006**, *128*, 5984.
- Sheldrick, G.M., *SHELX-97, Program for the Solution and Refinement of Crystal Structures*; University of Göttingen: Germany, 1997.
- (a) Rendle, D.F.; Trotter, J. *J. Chem. Soc. Perkin Trans.* **1974**, *2*, 847. (b) Roher, D.C.; Blessing, R.H.; Daux, W.L. *Acta Cryst.* **1979**, *B35*, 1244. (c) Minamikawa, J.; Rice, K.C.; Jacobsen, A.E.; Brossi, A. *J. Org. Chem.* **1980**, *45*, 1901. (d) Quattropiani, A.; Anderson, G.; Bernadinelli, G.; Kundig, E.P. *J. Am. Chem. Soc.* **1997**, *119*, 4773. (e) Nguyen, T.M.; Selfert, R.J.; Mowrey, D.R.; Lee, D. *Org. Lett.* **2002**, *4*, 3959. (f) Singh, V.; Iyer, S.R.; Mobin, S.M. *J. Org. Chem.* **2005**, *70*, 973.
- (a) Ensley, H.E.; Beggs, M.; Gao, Y. In *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L.A. Ed.; John Wiley & Sons, Ltd.: London, 1995; Vol. 3, pp. 3999–4000. (b) Oppolzer, W. *Angew. Chem. Int. Ed.* **1984**, *23*, 876. (c) Whitesell, J.K. *Chem. Rev.* **1992**, *92*, 953.
- (a) Kober, R.; Papadopoulos, K.; Miltz, W.; Enders, D.; Steglich, W. *Tetrahedron* **1985**, *41*, 1693. (b) Dyrbusch, M.; Egert, E. *Acta Cryst.* **1992**, *C48*, 2035. (c) Ebel, H.; Polborn, K.; Steglich, W. *Eur. J. Org. Chem.* **2002**, 2905. (d) Takagi, R.; Hashizume, M.; Nakamura, M.; Begum, S.; Hiraga, Y.; Kojima, S.; Ohkata, K. *J. Chem. Soc. Perkin Trans.* **2002**, *1*, 179. (e) Fustero, S.; Pina, B.; Salavert, E.; Navarro, A.; Ramirez de Arellano, M.C.; Fuentes, A.S. *J. Org. Chem.* **2002**, *67*, 4667. (f) Kulesza, A.; Mieczkowski, A.; Romanski, J.; Jurczak, J. *Tetrahedron: Asymmetry* **2003**, *14*, 1161. (g) Muniz, K.; Nieger, M.; Mansikkamaki, H. *Angew. Chem. Int. Ed.* **2003**, *42*, 5958. (h) Kudyba, I.; Raczko, J.; Jurczak, J. *J. Org. Chem.* **2004**, *69*, 2844.
- (a) Quinkert, G.; Schmalz, H.G.; Walzer, E.; Gross, S.; Duerner, Bats, J.W. *Angew. Chem. Int. Ed.* **1986**, *98*, 732. (b) Quinkert, G.; Schmalz, H.G.; Dzierzynski, E.; Duerner, Bats, J.W. *Angew. Chem. Int. Ed.* **1986**, *98*, 1023. (c) Quinkert, G.; Schmalz, H.G.; Walzer, E.; Gross, S.; Kowalczyk-Przewloka, T.; Schierloh, C.; Duerner, Bats, J.W. *Liebigs Ann.* **1988**, 283. (d) Inoue, T.; Kitagawa, O.; Ochiai, O.; Taguchi, T. *Tetrahedron: Asymmetry* **1995**, *6*, 691. (e) Amann, R.; Arnold, K.; Spitzner, D.; Majer, Z.; Snatzke, G. *Liebigs Ann.* **1996**, 349.
- (a) Borrione, E.; Prato, M.; Scorrano, G.; Stivanello, M.; Lucchini, V.; Valle, G. *J. Chem. Soc. Perkin Trans.* **1989**, *1*, 2245. (b) Timen, A. S.; Fischer, A.; Somfai, *Chem. Commun.* **2003**, 1150.