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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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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⁻³ 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,¹ we discovered that the reaction of (3-methylpentadienyl)Fe(CO)₃⁺ (**1**) with sodium malonates, followed by work up with NaHCO₃, gave 4,5-disubstituted cyclohexenones **2** (Scheme 1).² 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-diy)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.

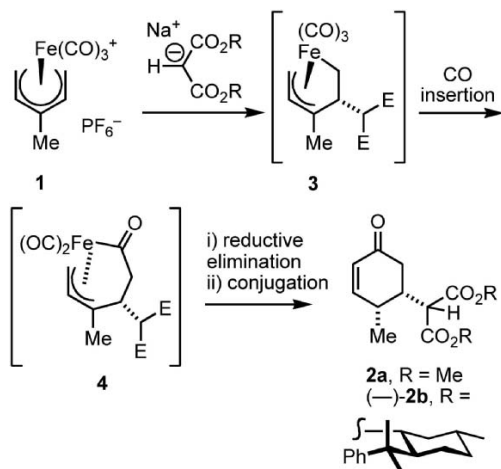
Experimental section

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 α radiation ($\lambda = 0.71073$ Å) and the $\Theta/2\Theta$ mode in the Θ 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 .³ 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)
β (°)	94.61(2)
Cell volume (Å ³)	2019.5(5)
Z	2
Density (calculated, g cm^{-3})	1.118
Absorption coefficient (mm^{-1})	0.072
Diffractometer	Bruker P4
Radiation	Mo $K\alpha$ ($\lambda = 0.71073$ Å)
θ 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 (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.⁴

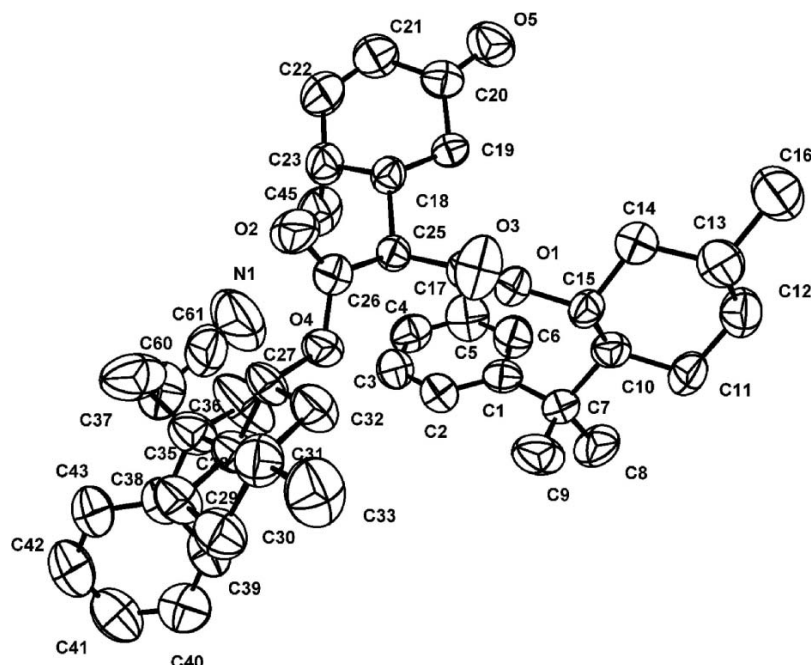


Fig. 1. ORTEP view of **2b** with crystallographic numbering scheme (50% probability ellipsoids).

Esters of 8-phenylmenthol have found use in diastereoselective transformations at either the α or β carbon.⁵ 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

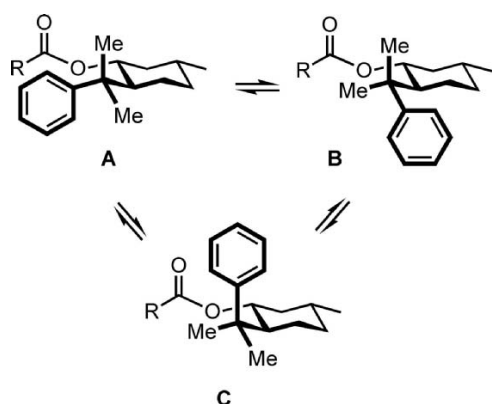


Fig. 2. Conformational possibilities for the side chain of 8-phenylmenthyl esters.

to the cyclohexane ring is observed in a number of crystal structures of (–)-8-phenylmenthyl esters.⁶ 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.⁷ 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,⁸ 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.

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