

(*RS,RS*)-5-[Hydroxy(4-methylphenyl)-methyl]furan-2(*5H*)-one

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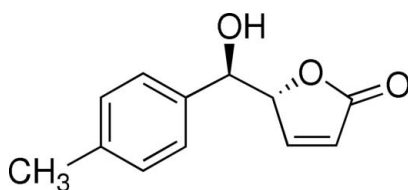
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.026; wR factor = 0.072; data-to-parameter ratio = 8.4.

The crystal structure of the racemic title compound, $\text{C}_{12}\text{H}_{12}\text{O}_3$, allowed the determination of the relative configuration at the two stereogenic centers. For the *R,R* isomer, the $\text{O}-\text{C}-\text{C}-\text{O}$ and $\text{C}-\text{C}-\text{C}-\text{C}$ torsion angles around the bond between the two methine C atoms are 62.38 (15) and -175.49 (13)°, respectively. The furan and tolyl groups are almost perpendicular, with a dihedral angle of 79.39 (5)°. Strong and linear intermolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonding ($\text{H}\cdots\text{O} = 2.04$ Å and $\text{O}-\text{H}\cdots\text{O} = 177^\circ$) is observed between the hydroxyl group and the $\text{C}=\text{O}$ oxygen.

Related literature

For information on bismuth(III)-catalyzed condensation reactions, see: Ollevier *et al.* (2005, 2006, 2007).



Experimental

Crystal data

$\text{C}_{12}\text{H}_{12}\text{O}_3$	$V = 978.89$ (11) Å ³
$M_r = 204.22$	$Z = 4$
Orthorhombic, $Pna2_1$	Mo $K\alpha$ radiation
$a = 8.9068$ (6) Å	$\mu = 0.10$ mm ⁻¹
$b = 5.9555$ (4) Å	$T = 100$ (2) K
$c = 18.4541$ (11) Å	$0.44 \times 0.24 \times 0.14$ mm

Data collection

Bruker SMART APEXII CCD diffractometer	7650 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2004)	1158 independent reflections
$T_{\min} = 0.948$, $T_{\max} = 0.986$	1139 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.014$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$	1 restraint
$wR(F^2) = 0.072$	H-atom parameters constrained
$S = 1.08$	$\Delta\rho_{\text{max}} = 0.25$ e Å ⁻³
1158 reflections	$\Delta\rho_{\text{min}} = -0.14$ e Å ⁻³
138 parameters	

Table 1

Selected torsion angles (°).

$\text{O2}-\text{C4}-\text{C5}-\text{O3}$	62.38 (15)	$\text{O3}-\text{C5}-\text{C6}-\text{C10}$	-164.99 (14)
$\text{C3}-\text{C4}-\text{C5}-\text{O3}$	-54.01 (18)	$\text{C4}-\text{C5}-\text{C6}-\text{C10}$	-42.46 (19)
$\text{O2}-\text{C4}-\text{C5}-\text{C6}$	-59.10 (16)	$\text{O3}-\text{C5}-\text{C6}-\text{C7}$	17.78 (19)
$\text{C3}-\text{C4}-\text{C5}-\text{C6}$	-175.49 (13)	$\text{C4}-\text{C5}-\text{C6}-\text{C7}$	140.31 (15)
$\text{H4}-\text{C4}-\text{C5}-\text{H5}$	-59		

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O3}-\text{H3A}\cdots\text{O1}^i$	0.84	2.04	2.8747 (17)	177

Symmetry code: (i) $x - \frac{1}{2}, -y + \frac{1}{2}, z$.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GK2106).

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supplementary materials

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Comment

In the context of our research on the bismuth(III)-catalyzed condensation reactions (Ollevier *et al.*, 2007; Ollevier *et al.*, 2005), we focused on the vinylogous Mukaiyama aldol of silyl dienol ethers with various aldehydes (Ollevier *et al.*, 2006). We carried out the reaction of 2-(trimethylsilyloxy)furan with *p*-tolualdehyde. The vinylogous Mukaiyama aldol reaction afforded 5-(hydroxy(4-tolyl)methyl)furan-2(*5H*)-one as the *syn* major diastereoisomer (*syn/anti* = 94:6) (Scheme 2). From the present crystallographic analysis of a racemic compound, the relative configuration at the two stereogenic centers (C4 and C5) was established (*4R,5R*) (Fig. 1) or (*4S,5S*).

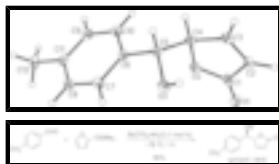
Experimental

To a solution of *p*-tolualdehyde (85 mg, 0.71 mmol) in diethyl ether (0.5 ml), was added Bi(OTf)₃·4H₂O (5.0 mg, 0.007 mmol). The mixture was brought to −78 °C, stirred at this temperature for 0.25 h, and a solution of 2-(trimethylsilyloxy)furan (133 mg, 0.85 mmol) in 0.5 ml of diethyl ether was added dropwise. The mixture was stirred at −78 °C until the reaction was completed as indicated by TLC. The reaction was diluted in tetrahydrofuran (1.0 ml) and quenched with 10% aqueous HCl (1.0 ml). The mixture was stirred for 0.25 h at room temperature, neutralized by addition of a saturated aqueous NaHCO₃ solution, and extracted with ethyl acetate. The organic phases were combined, dried over Na₂SO₄, and concentrated under reduced pressure (rotary evaporator). The *syn/anti* ratio (94:6) was determined by ¹H NMR analysis of the crude product (δ major: 4.66 p.p.m., δ minor: 5.03 p.p.m.). The residue was purified by silica gel chromatography (25% ethyl acetate/hexane) to afford 130 mg (90%) of the pure *syn* diastereoisomer (white solid). The product was recrystallized (hexane/ethyl acetate) to afford the title compound as white crystals.

Refinement

The H atoms were generated geometrically with C—H and O—H distances of 0.95 – 1.00 Å and 0.84 Å respectively, and were included in the refinement in the riding model approximation; their temperature factors were set to 1.5 times those of the equivalent isotropic temperature factors of the parent site (methyl) and 1.2 times for others. Due to weak anomalous scattering effects of the light atoms with Mo radiation, Friedel pairs were merged.

Figures



(*RS,RS*)-5-[Hydroxy(4-methylphenyl)methyl]furan-2(5*H*)-one

Crystal data

$C_{12}H_{12}O_3$	$D_x = 1.386 \text{ Mg m}^{-3}$
$M_r = 204.22$	Melting point: 413 K
Orthorhombic, $Pna2_1$	Mo $K\alpha$ radiation
Hall symbol: P 2c -2n	$\lambda = 0.71073 \text{ \AA}$
$a = 8.9068 (6) \text{ \AA}$	Cell parameters from 5985 reflections
$b = 5.9555 (4) \text{ \AA}$	$\theta = 2.2\text{--}28.1^\circ$
$c = 18.4541 (11) \text{ \AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$V = 978.89 (11) \text{ \AA}^3$	$T = 100 (2) \text{ K}$
$Z = 4$	Rectangular, colorless
$F_{000} = 432$	$0.44 \times 0.24 \times 0.14 \text{ mm}$

Data collection

Bruker SMART APEXII CCD diffractometer	1158 independent reflections
Radiation source: fine-focus sealed tube	1139 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.014$
$T = 100(2) \text{ K}$	$\theta_{\text{max}} = 27.5^\circ$
ω scans	$\theta_{\text{min}} = 2.2^\circ$
Absorption correction: multi-scan (SADABS; Sheldrick, 2004)	$h = -11 \rightarrow 11$
$T_{\text{min}} = 0.948$, $T_{\text{max}} = 0.986$	$k = -7 \rightarrow 7$
7650 measured reflections	$l = -23 \rightarrow 23$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.026$	$w = 1/[\sigma^2(F_o^2) + (0.0489P)^2 + 0.1853P]$
$wR(F^2) = 0.072$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{\text{max}} = 0.001$
1158 reflections	$\Delta\rho_{\text{max}} = 0.25 \text{ e \AA}^{-3}$
138 parameters	$\Delta\rho_{\text{min}} = -0.14 \text{ e \AA}^{-3}$
1 restraint	Extinction correction: none
Primary atom site location: structure-invariant direct methods	
Secondary atom site location: difference Fourier map	

Special details

Experimental. Mp 140 °C; $R_f = 0.20$ (30% ethyl acetate/hexane); ^1H NMR (400 MHz, CDCl_3): $\delta = 7.25$ (d, $J = 7.6$ Hz, 2H), 7.21 (d, $J = 7.6$ Hz, 2H), 7.13 (dd, $J = 5.9, 1.6$ Hz, 1H), 6.12 (dd, $J = 5.9, 2.0$ Hz, 1H), 5.13–5.16 (m, 2H), 4.66 (d, $J = 7.2$ Hz, 1H), 2.80 (br s, 1H), 2.36 (s, 3H); RMN ^{13}C (100 MHz, CDCl_3): $\delta = 172.6, 153.4, 139.1, 134.9, 129.7, 126.9, 123.2, 87.2, 75.8, 21.5$; IR (KBr): 3411, 1742 cm^{-1} ; HRMS: Calcd for $\text{C}_{12}\text{H}_{12}\text{O}_3$ (M^+) 204.0786, found 204.0782.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.50432 (13)	0.5539 (2)	0.67957 (7)	0.0191 (3)
C1	0.38910 (18)	0.5085 (2)	0.64822 (10)	0.0153 (3)
O2	0.39225 (12)	0.43751 (19)	0.57840 (6)	0.0146 (2)
C2	0.23233 (18)	0.5146 (3)	0.67242 (10)	0.0164 (3)
H2	0.1986	0.5591	0.7191	0.020*
C3	0.14558 (18)	0.4476 (3)	0.61813 (10)	0.0159 (3)
H3	0.0392	0.4373	0.6197	0.019*
C4	0.24068 (17)	0.3909 (3)	0.55420 (9)	0.0144 (3)
H4	0.2147	0.4927	0.5130	0.017*
C5	0.23120 (17)	0.1448 (3)	0.52891 (8)	0.0141 (3)
H5	0.1268	0.1152	0.5115	0.017*
O3	0.26211 (13)	−0.00292 (19)	0.58730 (7)	0.0175 (3)
H3A	0.1863	−0.0119	0.6142	0.026*
C6	0.33994 (16)	0.0935 (3)	0.46734 (8)	0.0142 (3)
C7	0.41772 (18)	−0.1102 (3)	0.46543 (9)	0.0171 (3)
H7	0.4074	−0.2135	0.5043	0.021*
C8	0.51017 (18)	−0.1631 (3)	0.40711 (9)	0.0187 (3)
H8	0.5611	−0.3033	0.4067	0.022*
C9	0.4542 (2)	0.1892 (3)	0.35204 (9)	0.0196 (3)
H9	0.4669	0.2940	0.3137	0.023*
C10	0.36031 (18)	0.2425 (3)	0.40992 (9)	0.0178 (3)
H10	0.3094	0.3827	0.4103	0.021*
C11	0.52985 (19)	−0.0159 (3)	0.34946 (9)	0.0177 (3)
C12	0.6291 (2)	−0.0768 (3)	0.28616 (10)	0.0250 (4)
H12A	0.5777	−0.1873	0.2556	0.038*
H12B	0.7234	−0.1409	0.3041	0.038*
H12C	0.6507	0.0582	0.2576	0.038*

supplementary materials

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0148 (5)	0.0221 (6)	0.0205 (6)	-0.0026 (5)	-0.0003 (4)	-0.0030 (5)
C1	0.0189 (8)	0.0103 (6)	0.0168 (7)	0.0008 (5)	0.0027 (6)	0.0001 (5)
O2	0.0113 (5)	0.0165 (5)	0.0159 (5)	-0.0011 (4)	0.0019 (4)	-0.0003 (4)
C2	0.0166 (7)	0.0144 (7)	0.0182 (7)	0.0011 (5)	0.0044 (6)	0.0001 (6)
C3	0.0151 (7)	0.0126 (7)	0.0198 (7)	0.0011 (6)	0.0029 (6)	0.0028 (6)
C4	0.0108 (7)	0.0157 (7)	0.0167 (7)	0.0005 (5)	-0.0001 (5)	0.0017 (6)
C5	0.0122 (7)	0.0157 (7)	0.0145 (7)	-0.0001 (5)	0.0011 (6)	0.0012 (6)
O3	0.0168 (5)	0.0184 (6)	0.0174 (6)	0.0020 (4)	0.0041 (5)	0.0054 (5)
C6	0.0115 (6)	0.0164 (7)	0.0148 (7)	-0.0016 (5)	-0.0011 (6)	-0.0016 (6)
C7	0.0173 (7)	0.0142 (7)	0.0199 (7)	-0.0016 (6)	0.0006 (6)	0.0006 (6)
C8	0.0186 (7)	0.0153 (7)	0.0223 (8)	0.0003 (6)	-0.0009 (6)	-0.0034 (6)
C9	0.0221 (8)	0.0214 (8)	0.0152 (7)	-0.0010 (7)	0.0001 (6)	0.0005 (6)
C10	0.0181 (7)	0.0172 (7)	0.0181 (7)	0.0026 (6)	-0.0013 (6)	0.0016 (7)
C11	0.0169 (8)	0.0209 (8)	0.0152 (7)	-0.0031 (6)	0.0004 (6)	-0.0059 (6)
C12	0.0278 (9)	0.0277 (9)	0.0196 (8)	0.0001 (7)	0.0060 (7)	-0.0066 (7)

Geometric parameters (\AA , $^\circ$)

O1—C1	1.209 (2)	C6—C10	1.394 (2)
C1—O2	1.356 (2)	C6—C7	1.397 (2)
C1—C2	1.466 (2)	C7—C8	1.391 (2)
O2—C4	1.4489 (18)	C7—H7	0.9500
C2—C3	1.327 (3)	C8—C11	1.390 (2)
C2—H2	0.9500	C8—H8	0.9500
C3—C4	1.491 (2)	C9—C10	1.393 (2)
C3—H3	0.9500	C9—C11	1.396 (2)
C4—C5	1.541 (2)	C9—H9	0.9500
C4—H4	1.0000	C10—H10	0.9500
C5—O3	1.4179 (19)	C11—C12	1.509 (2)
C5—C6	1.524 (2)	C12—H12A	0.9800
C5—H5	1.0000	C12—H12B	0.9800
O3—H3A	0.8400	C12—H12C	0.9800
O1—C1—O2	120.45 (15)	C10—C6—C5	121.47 (14)
O1—C1—C2	131.09 (16)	C7—C6—C5	120.51 (14)
O2—C1—C2	108.46 (14)	C8—C7—C6	120.64 (15)
C1—O2—C4	109.47 (12)	C8—C7—H7	119.7
C3—C2—C1	108.50 (15)	C6—C7—H7	119.7
C3—C2—H2	125.8	C11—C8—C7	121.59 (15)
C1—C2—H2	125.8	C11—C8—H8	119.2
C2—C3—C4	109.56 (14)	C7—C8—H8	119.2
C2—C3—H3	125.2	C10—C9—C11	121.03 (15)
C4—C3—H3	125.2	C10—C9—H9	119.5
O2—C4—C3	104.00 (13)	C11—C9—H9	119.5
O2—C4—C5	109.07 (12)	C9—C10—C6	121.05 (14)

C3—C4—C5	115.09 (13)	C9—C10—H10	119.5
O2—C4—H4	109.5	C6—C10—H10	119.5
C3—C4—H4	109.5	C8—C11—C9	117.71 (15)
C5—C4—H4	109.5	C8—C11—C12	120.98 (15)
O3—C5—C6	108.60 (12)	C9—C11—C12	121.31 (15)
O3—C5—C4	110.45 (12)	C11—C12—H12A	109.5
C6—C5—C4	112.43 (12)	C11—C12—H12B	109.5
O3—C5—H5	108.4	H12A—C12—H12B	109.5
C6—C5—H5	108.4	C11—C12—H12C	109.5
C4—C5—H5	108.4	H12A—C12—H12C	109.5
C5—O3—H3A	109.5	H12B—C12—H12C	109.5
C10—C6—C7	117.96 (14)		
O1—C1—O2—C4	178.96 (14)	O3—C5—C6—C10	-164.99 (14)
C2—C1—O2—C4	-0.91 (16)	C4—C5—C6—C10	-42.46 (19)
O1—C1—C2—C3	-179.55 (17)	O3—C5—C6—C7	17.78 (19)
O2—C1—C2—C3	0.31 (17)	C4—C5—C6—C7	140.31 (15)
C1—C2—C3—C4	0.41 (18)	C10—C6—C7—C8	-1.2 (2)
C1—O2—C4—C3	1.11 (16)	C5—C6—C7—C8	176.12 (14)
C1—O2—C4—C5	-122.16 (13)	C6—C7—C8—C11	0.7 (2)
C2—C3—C4—O2	-0.92 (17)	C11—C9—C10—C6	0.5 (3)
C2—C3—C4—C5	118.32 (15)	C7—C6—C10—C9	0.6 (2)
O2—C4—C5—O3	62.38 (15)	C5—C6—C10—C9	-176.71 (15)
C3—C4—C5—O3	-54.01 (18)	C7—C8—C11—C9	0.4 (2)
O2—C4—C5—C6	-59.10 (16)	C7—C8—C11—C12	-179.29 (15)
C3—C4—C5—C6	-175.49 (13)	C10—C9—C11—C8	-1.0 (2)
H4—C4—C5—H5	-59	C10—C9—C11—C12	178.67 (16)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O3—H3A...O1 ⁱ	0.84	2.04	2.8747 (17)	177

Symmetry codes: (i) $x-1/2, -y+1/2, z$.

Fig. 1

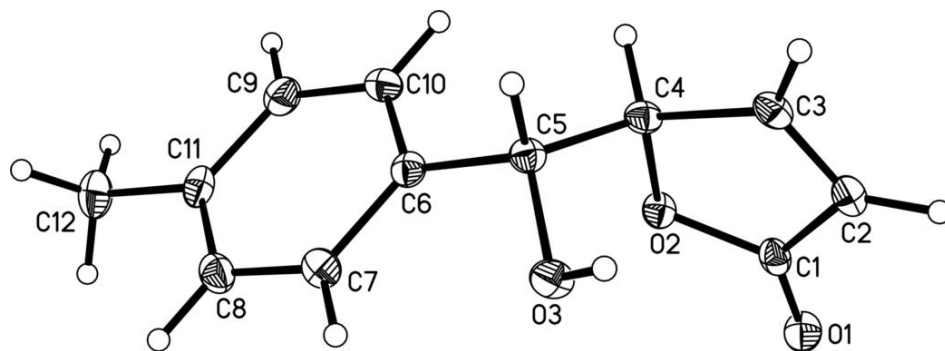


Fig. 2

