

*meso*-4,5-Dihydroxy-4,5-dimethylocta-1,7-diyneMichael Bolte,<sup>a</sup> Klaus Eckstein<sup>a</sup>  
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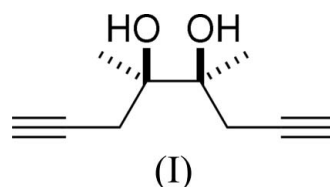
## Key indicators

Single-crystal X-ray study  
*T* = 173 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$   
*R* factor = 0.048  
*wR* factor = 0.130  
Data-to-parameter ratio = 25.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Molecules of the title compound,  $\text{C}_{10}\text{H}_{14}\text{O}_2$ , are connected by intermolecular hydrogen bonds, forming zigzag chains running in the *b*-axis direction. In addition, the two hydroxyl groups form an intramolecular hydrogen bond.

## Comment

Allenyl methyl ketone is an important allenic building block for organic synthesis (Schuster & Coppola, 1984; Krause & Hashmi, 2004; Hashmi *et al.*, 1997, 2000). However, significant amounts of by-products are formed, even in the most efficient of the reported syntheses (Buono & Llinas, 1981; Buono, 1981; Hussain & Agosta, 1981). As a new route, we selected diacetyl as the starting material which, after the addition of two equivalents of propargyl magnesium bromide (Brandsma, 1988), should deliver the title compound, (I). A subsequent glycol cleavage with periodic acid (Elks *et al.*, 1954) should then provide methyl propargyl ketone, which was expected to finally isomerize to allenyl methyl ketone when treated with a mild base (Hashmi *et al.*, 1998; for a general treatment of these isomerizations, see Krause & Hashmi, 2004). Unfortunately, periodate failed in the oxidative cleavage; only the problematic reagent lead(IV) acetate gave the desired reaction, which synthetically was not a step forward.

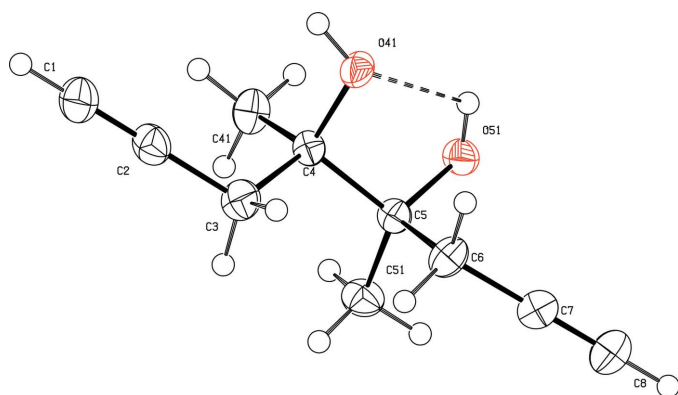


A perspective view of (I) is shown in Fig. 1. Bond lengths and angles can be regarded as normal (Cambridge Structural Database, Version 1.6 plus three updates; *MOGUL* Version 1.0; Allen, 2002). (I) is a *meso*-compound with opposite configurations of the two chiral centres. The molecular conformation of (I) is determined by an intramolecular hydrogen bond (Table 2). The two hydroxyl groups are in a synclinal orientation. On the other hand, an antiperiplanar conformation is found for atoms C2, C5 and C4, C7 (Table 1). In the crystal structure, the molecules form hydrogen-bonded zigzag chains running in the *b*-axis direction (Fig. 2).

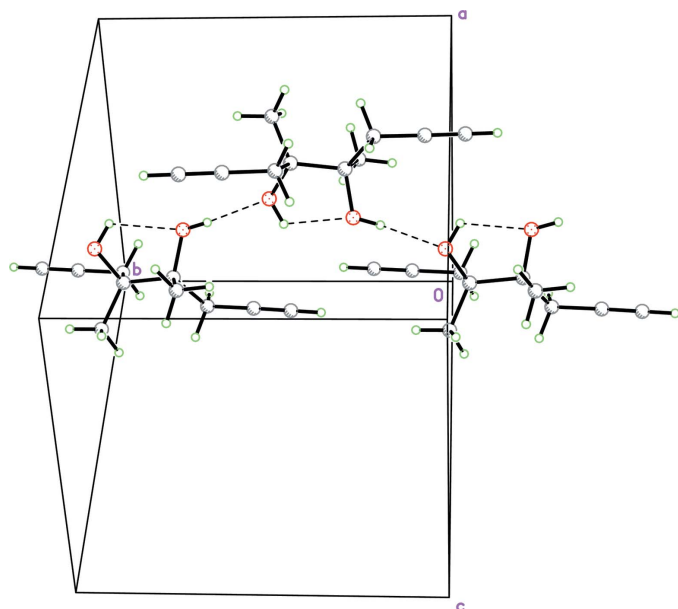
## Experimental

Following a general procedure of Brandsma (1988) for the addition of allenyl magnesium bromide to carbonyl compounds and after a purification by column chromatography on silica gel (hexanes–ethyl acetate 5:2 *v/v*), a 43% yield of a 1:1 mixture of both diastereomers of

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**Figure 1**  
A perspective view of the title compound with the atom numbering; displacement ellipsoids are drawn at the 50% probability level. The intramolecular hydrogen bond is drawn as a dashed line.



**Figure 2**  
A partial packing diagram of the title compound, showing the hydrogen bonds as dashed lines.

the title compound was obtained. This mixture could be separated by preparative HPLC. *syn*-Diastereomer (m.p. 308–310 K): IR (film, KBr): 3523, 3448, 3292, 2985, 2946, 2117, 1458, 1426, 1381, 1355, 1232, 1138, 1072, 953  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 250 MHz):  $\delta$  2.75 (*dd*,  $J = 16.7$  Hz, 2.7 Hz, 2H), 2.63 (*s*, 2H), 2.45 (*dd*,  $J = 16.7$  Hz, 2.7 Hz, 2H), 2.11 (*t*,  $J = 2.7$  Hz, 2H), 1.32 (*s*, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 62.9 MHz):  $\delta$  80.9 (quart. C, 2C), 75.1 (quart. C, 2C), 71.4 (CH, 2C), 27.6 ( $\text{CH}_3$ , 2C), 21.6 ( $\text{CH}_2$ , 2C). Elemental analysis calculated for  $\text{C}_{10}\text{H}_{14}\text{O}_2$ : C 72.26, H 8.49%; found: C 72.08, H 8.40%. *meso*-Diastereomer (m.p. 306–308 K): IR (film, KBr): 3533, 3446, 3294, 2984, 2943, 2117, 1452, 1424, 1376, 1356, 1236, 1112, 1074, 936  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 250 MHz):  $\delta$  2.64 (*ddd*,  $J = 16.6$  Hz, 2.7 Hz, 0.5 Hz, 2H), 2.57 (*s*, 2H), 2.43 (*dd*,  $J = 16.7$  Hz, 2.7 Hz, 2H), 2.12 (*t*,  $J = 2.7$  Hz, 2H), 1.38 (*d*,  $J = 0.5$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 62.9 MHz):  $\delta$  80.6 (quart. C, 2C), 75.1 (quart. C, 2C), 71.6 (CH, 2C), 27.6 ( $\text{CH}_3$ , 2C), 22.2 ( $\text{CH}_2$ , 2C). Elemental analysis calculated for  $\text{C}_{10}\text{H}_{14}\text{O}_2$ : C 72.26, H 8.49%; found: C 72.00, H 8.46%. Single crystals of the title compound were grown by slow evaporation of a solution in diethyl ether.

### Crystal data

$\text{C}_{10}\text{H}_{14}\text{O}_2$   
 $M_r = 166.21$   
Monoclinic,  $P2_1/c$   
 $a = 8.750$  (2) Å  
 $b = 10.120$  (2) Å  
 $c = 11.394$  (2) Å  
 $\beta = 107.25$  (3)°  
 $V = 963.6$  (4) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.146$  Mg m<sup>-3</sup>  
Mo  $K\alpha$  radiation  
Cell parameters from 8192 reflections  
 $\theta = 3.2$ – $24.5^\circ$   
 $\mu = 0.08$  mm<sup>-1</sup>  
 $T = 173$  (2) K  
Block, colourless  
 $0.47 \times 0.41 \times 0.32$  mm

### Data collection

Siemens SMART CCD three-circle diffractometer  
 $\omega$  scans  
Absorption correction: none  
20872 measured reflections  
2802 independent reflections

2245 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.029$   
 $\theta_{\text{max}} = 31.4^\circ$   
 $h = -12 \rightarrow 12$   
 $k = -14 \rightarrow 13$   
 $l = -15 \rightarrow 15$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.048$   
 $wR(F^2) = 0.130$   
 $S = 1.07$   
2802 reflections  
111 parameters  
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0582P)^2 + 0.3195P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.33$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.22$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

C1–C2	1.188 (2)	C5–O51	1.4395 (14)
C4–O41	1.4308 (14)	C7–C8	1.1920 (19)
C2–C3–C4–C5	−170.80 (11)	C4–C5–C6–C7	−171.71 (10)
O41–C4–C5–O51	−53.73 (11)		

**Table 2**

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O41–H41 $\cdots$ O51 <sup>i</sup>	0.84	1.98	2.8071 (12)	166
O51–H51 $\cdots$ O41	0.84	2.17	2.6298 (13)	115

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

H atoms were located in a difference electron density map, but refined with fixed individual displacement parameters [ $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{O})$  or  $1.5U_{\text{eq}}(\text{methyl C})$ ] using a riding-model, with C–H = 0.95–0.99 Å and O–H = 0.84 Å. In addition, the torsion angles about the C–O bonds of the hydroxy groups were refined.

Data collection: SMART (Siemens, 1995); cell refinement: SAINT (Siemens, 1995); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: XP in SHELXTL-Plus (Sheldrick, 1991) and PLATON (Spek, 2003); software used to prepare material for publication: SHELXL97 and PLATON.

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### References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.  
Brandsma, L. (1988). *Preparative Acetylenic Chemistry*, pp. 95–96. Amsterdam: Elsevier.

- Buono, G. (1981). *Synthesis*, pp. 872–872.
- Buono, G. & Llinas, J. R. (1981). *J. Am. Chem. Soc.* **103**, 4532–4540.
- Elks, J., Phillipps, G. H., Taylor, D. A. H. & Wyman, L. J. (1954). *J. Chem. Soc.* pp. 1739–1749.
- Hashmi, A. S. K., Bats, J. W., Choi, J.-H. & Schwarz, L. (1998). *Tetrahedron Lett.* **39**, 7491–7494.
- Hashmi, A. S. K., Ruppert, T. L., Knöfel, T. & Bats, J. W. (1997). *J. Org. Chem.* **62**, 7295–7304.
- Hashmi, A. S. K., Schwarz, L., Choi, J.-H. & Frost, T. M. (2000). *Angew. Chem. Int. Ed.* **39**, 2285–2288.
- Hussain, S. & Agosta, W. C. (1981). *Tetrahedron*, **37**, 3301–3306.
- Krause, N. & Hashmi, A. S. K. (2004). *Modern Allene Chemistry*, pp. 3–50. Weinheim: Wiley-VCH.
- Schuster, H. F. & Coppola, G. M. (1984). *Allenenes in Organic Chemistry*. New York: Wiley.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Siemens (1995). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.