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2-Hydroxy-5,5-dimethylcyclohex-2-en-1-one

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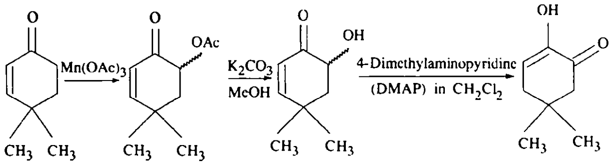
Abstract

The structure of the title compound, $C_8H_{12}O_2$, which is a rearrangement product of the reaction of 6-hydroxy-4,4-dimethylcyclohex-2-en-1-one and 4-dimethylaminopyridine has been identified as 2-hydroxy-5,5-dimethylcyclohex-2-en-1-one. The C atom of the six-membered ring connected to the two methyl groups is 0.617 (2) Å out of the least-squares plane defined by the other C atoms of the ring. The unit cell consists of discrete molecules with intra- and intermolecular hydrogen bonds.

Comment

Quassinoids is a group of organic molecules with potent anticancer properties (Kupchan *et al.*, 1975; Kupchan & Lacadie, 1975; Wani *et al.*, 1979). In the synthesis of quassinoids such as castenolide (Grieco, Ferrino & Jaw, 1982) and quassin (Vidari, Ferrino & Grieco, 1984), the formation of the diosphenol ring is of interest. In connection with the studies on diosphenol ring formation, a new preparative method has been developed. As a model compound, 6-hydroxy-4,4-dimethylcyclohex-2-en-1-one was chosen. This model compound was obtained by using a mild oxidizing agent $Mn(OAc)_3$ and subsequent hydrolysis with K_2CO_3. A rearrangement reaction of the model compound with the bulky mild base 4-dimethylaminopyridine (DMAP) produced the target compound 2-hydroxy-5,5-dimethylcyclohex-2-en-1-one, (I). The resultant target compound might have possibly one ketonic and two keto-enolic tautomeric forms. The structure of the rearrangement product has been determined to define the actual tautomeric form.



(I)

The six-membered ring of the title molecule is not planar (Fig. 1). The C5 atom of the ring, connected with the two methyl groups, is 0.617 (2) Å out of the least-squares plane defined by the other C atoms of the ring. The distances of the O1 and O2 atoms from the best plane described above are 0.089 (2) and −0.016 (2) Å, respectively. The bond angles within the ring are in the range 108.7 (2)–123.1 (2)°, the smallest value belonging to C4—C5—C6. The bond angles around C5 ranging from 108.7 (2) to 110.3 (2)° are in agreement with tetrahedral bond values. C2—C3 [1.320 (4) Å] and C1—O1 [1.227 (3) Å] are both double bonds, all other bonds are in the single-bond range. The molecules oriented approximately parallel to the diagonals of the *bc* plane of the unit cell are stacked along the *b* axis with an intermolecular hydrogen bond between O1 and O2 ($-x$, $1-y$, $1-z$). There is also an intramolecular hydrogen bond in the molecule between O1 and O2. Details are given in Table 2. Similar ring structures, studied with spectroscopic techniques, are reported for some intermediate products in steroid synthesis (Kurath, 1967) and in toxodione (Stevens & Bisacchi, 1982). No X-ray structure determinations are available for these compounds.

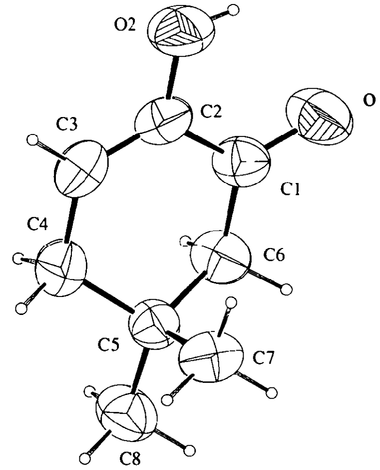


Fig. 1. The molecular structure (*ORTEP*II; Johnson, 1976) of (I) with the atomic numbering scheme. The displacement ellipsoids are drawn at the 50% probability. H atoms are shown as small circles of arbitrary radii.

Experimental

A mixture of $Mn(OAc)_3$ hydrate (4.2 g, 18.0 mmol) in benzene (200 ml) was refluxed for 45 min. The mixture was cooled to 298 K and 4,4-dimethylcyclohex-2-en-1-one (1.5 g, 12.08 mmol) was gradually added. The mixture was allowed to reflux until the dark brown colour disappeared. The reaction mixture was diluted with an equal amount of ethyl acetate and the organic phase was washed with 1 *N* HCl (3 × 100 ml) followed by saturated $NaHCO_3$ (3 × 100 ml) and brine (3 × 50 ml). The organic phase was dried over $MgSO_4$ and evaporated *in vacuo*. The crude product was separated by flash column chromatography using ethyl acetate–hexane

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(1:4) as eluent to afford 6-acetoxy-4,4-dimethylcyclohex-2-en-1-one (Demir & Jeganathan, 1991) which was subsequently hydrolyzed by K_2CO_3 in MeOH according to a standard literature procedure (Tanyeli, Demir & Dikici, 1996). Hydrolysis product 2-hydroxy-5,5-dimetylcyclohex-2-en-1-one (0.7 g, 4.99 mmol) was subjected to the rearrangement reaction by 4-dimethylaminopyridine (0.61 g, 4.99 mmol) in CH_2Cl_2 (25 ml) to yield 2-hydroxy-5,5-dimethylcyclohex-2-en-1-one (Langin-Lanteri & Huet, 1976) (0.62 g, 89%). The product was purified by flash column chromatography using ethyl acetate–hexane (1:4) as eluent. Crystals were grown by slow evaporation of ethyl acetate solutions. Air sensitive crystals were sealed for data collection.

Crystal data

$C_8H_{12}O_2$
$M_r = 140.18$
Monoclinic
$P2_1/n$
$a = 10.640\,(2)$ Å
$b = 5.987\,(2)$ Å
$c = 12.726\,(3)$ Å
$\beta = 104.556\,(3)°$
$V = 784.7\,(4)$ Å^3
$Z = 4$
$D_x = 1.1865$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10.28–18.31°$
$\mu = 0.078$ mm^{-1}
$T = 294$ K
Prism
$0.40 \times 0.30 \times 0.25$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1519 measured reflections
1448 independent reflections
943 reflections with $I > \sigma(I)$
$R_{\rm int} = 0.010$

$\theta_{\rm max} = 25.01°$
$h = -12 \rightarrow 12$
$k = 0 \rightarrow 7$
$l = 0 \rightarrow 15$
3 standard reflections
frequency: 120 min
intensity decay: not corrected

Refinement

Refinement on F
$R = 0.048$
$wR = 0.054$
$S = 0.85$
943 reflections
94 parameters
$w = 1/[\sigma F^2 + (0.02F)^2 + 1.0]$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.138$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.129$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

O1—C1	1.227 (3)	C3—C4	1.490 (4)
O2—C2	1.368 (3)	C4—C5	1.524 (3)
C1—C2	1.462 (3)	C5—C6	1.528 (4)
C1—C6	1.493 (4)	C5—C7	1.519 (4)
C2—C3	1.320 (4)	C5—C8	1.524 (4)
O1—C1—C2	119.9 (2)	C4—C5—C6	108.7 (2)
O1—C1—C6	122.3 (2)	C4—C5—C7	110.3 (2)
C2—C1—C6	117.8 (2)	C4—C5—C8	110.3 (2)
O2—C2—C1	117.3 (2)	C6—C5—C7	108.9 (2)
O2—C2—C3	121.6 (2)	C6—C5—C8	109.8 (2)
C1—C2—C3	121.1 (2)	C7—C5—C8	108.8 (2)
C2—C3—C4	123.1 (2)	C1—C6—C5	113.6 (2)
C3—C4—C5	113.8 (2)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O1	0.83	2.25	2.704 (3)	115
O2—H2···O1$^{\rm i}$	0.83	2.05	2.787 (3)	148

Symmetry code: (i) $-x, 1-y, 1-z$.

H atoms were placed geometrically 0.95 Å from the parent C atoms, refined for a few cycles and a riding model was used for these H atoms with $U_{\rm iso}(\rm H) = 1.3U_{\rm eq}(\rm C)$. The H atom of the hydroxyl group was found from a difference map and refined with $U_{\rm eq}(\rm H) = 1.3U_{\rm eq}(\rm O)$.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1993). Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SIR* in *MolEN*. Program(s) used to refine structure: *LSFM* in *MolEN*. Molecular graphics: *MolEN* version of *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN* and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1495). Services for accessing these data are described at the back of the journal.

References

Demir, A. S. & Jeganathan, A. (1991). *Synthesis*, pp. 235–247.
Enraf–Nonius (1993). *CAD*-4 *EXPRESS*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
Grieco, P. A., Ferrino, R. L. S. & Jaw, J. Y. (1982). *J. Org. Chem.* **47**, 601–602.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Kupchan, S. M., Britton, R. W., Lacadie, J. A., Ziegler, M. F. & Sigel, C. W. (1975). *J. Org. Chem.* **40**, 648–654.
Kupchan, S. M. & Lacadie, J. A. (1975). *J. Org. Chem.* **40**, 654–656.
Kurath, P. (1967). *J. Org. Chem.* **32**, 3626–3635.
Langin-Lanteri, M. T. & Huet, J. (1976). *Synthesis*, pp. 541–543.
Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.
Stevens, R. X. & Bisacchi, G. S. (1982). *J. Org. Chem.* **47**, 2396–2399.
Tanyeli, C., Demir, A. S. & Dikici, E. (1996). *Tetrahedron Asymm.* **7**, 2399–2402.
Vidari, G., Ferrino, S. & Grieco, P. A. (1984). *J. Am. Chem. Soc.* **106**, 3539–3548.
Wani, M. C., Tayler, H. L., Thompson, J. B., Wall, M. E., McPhail, A. T. & Onan, K. D. (1979). *Tetrahedron*, **35**, 17–24.