

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *MULTAN11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

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Structure of a 2-Acylyndan-1-one

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Abstract

2-(1-Hydroxyethylidene)indan-1-one exists as the enol form and is nearly planar with a maximum deviation from the least-squares plane of all non-H atoms of 0.045 (2) Å. The molecule has a *Z* configuration about the enol double bond. The hydroxyl H atom forms an intramolecular hydrogen bond to the carbonyl O atom, having an O...O distance of 2.610 (2) Å and an angle about the H atom of 150 (2)°. The C(=O)—C=C—O torsion angle about the enol double bond has a magnitude of 1.9 (2)°. The C=O and C=C distances are 1.257 (2) and 1.359 (2) Å, respectively.

Comment

The synthesis of some derivatives of atipamezol (Garcia & Enas, 1992), required in our laboratory, involved the preparation of (*Z*)-2-acylyndan-1-one as an intermediate. It was prepared by condensing phthalaldehyde with acetone in aqueous potassium hydroxide (Thiele & Falk, 1906). Bright yellow crystals were grown by slow evaporation from an ethanol–tetrahydrofuran mixture (1:2); m.p. 337–340 K. Studies performed by Forsén, Merényi & Nilsson (1964) suggested that 2-acylyndan-1,3-diones exist exclusively in the enol form, which had been partially confirmed by the X-ray diffraction study of Csöregi & Norrestam (1976). A more precise study by Korp, Bernal & Lemke (1980) confirmed the enol form with an intramolecular hydrogen bond, H...O 1.56 (5) Å. This result is similar to that found for

(*Z*)-2-acylyndan-1-one; H...O 1.69 (2) Å. The occurrence of the title compound in the enol form agrees with similar results for the parent compounds 2-pivaloylyndan-1,3-dione and 2-acylyndan-1,3-dione (Korp, Bernal & Lemke, 1980). Structural data for 2-pivaloylyndan-1,3-dione and 2-acylyndan-1,3-dione (Korp, Bernal & Lemke, 1980) are in agreement with those of the title compound. The configuration at the C9=C10 double bond has been determined to be *Z* according to the Cahn–Ingold–Prelog convention (Cahn, Ingold & Prelog, 1956).

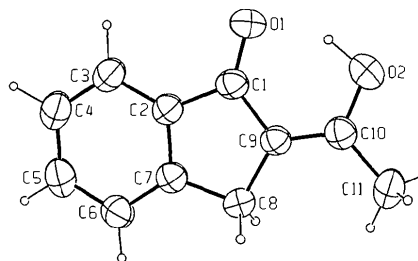


Fig. 1. ORTEP drawing (Johnson, 1965) of the molecule, representing heavy atoms as 40% probability ellipsoids and H atoms as circles of arbitrary radii.

Experimental

Crystal data

C₁₁H₁₀O₂
M_r = 174.2
 Monoclinic
*P*2₁/*n*
a = 7.2980 (3) Å
b = 16.0475 (8) Å
c = 7.9701 (3) Å
 β = 108.289 (4)°
V = 886.3 (2) Å³
Z = 4
D_x = 1.305 Mg m⁻³

Mo K α radiation
 λ = 0.71073 Å
 Cell parameters from 25 reflections
 θ = 10–12°
 μ = 0.08 mm⁻¹
T = 298 K
 Needle fragment
 0.50 × 0.37 × 0.28 mm
 Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω -2 θ scans
 Absorption correction: none
 2667 measured reflections
 2347 independent reflections
 1490 observed reflections
 $[I > 3\sigma(I)]$

R_{int} = 0.014
 θ_{\max} = 29°
h = 0 → 9
k = 0 → 21
l = -10 → 10
 3 standard reflections
 frequency: 167 min
 intensity variation: <2%

Refinement

Refinement on *F*
 Final *R* = 0.039
wR = 0.047
S = 2.261
 1490 reflections
 159 parameters

$\Delta\rho_{\max}$ = 0.17 e Å⁻³
 $\Delta\rho_{\min}$ = -0.11 e Å⁻³
 Extinction correction: (1 + *gI_c*)⁻¹ applied to *F_c*
 Extinction coefficient: *g* = 2.7 (2) × 10⁻⁶

All H-atom parameters re-fined
 $w = 4F_o^2[\sigma^2(I) + (0.02F_o^2)^2]^{-1}$
 $(\Delta/\sigma)_{\max} = 0.03$

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
 Korp, J. D., Bernal, I. & Lemke, T. L. (1980). *Acta Cryst.* B36, 428–434.
 Thiele, J. & Falk, K. G. (1906). *Liebigs Ann. Chem.* 347, 112–131.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)

$$B_{eq} = (8\pi^2/3)\sum_i\sum_j B_{ij}a_i^*a_j^*a_i.a_j.$$

	x	y	z	B_{eq}
O1	0.2873 (1)	−0.09367 (6)	0.5641 (1)	5.53 (3)
O2	0.5932 (2)	−0.18533 (7)	0.6025 (2)	5.85 (3)
C1	0.4041 (2)	−0.04253 (8)	0.6606 (2)	4.07 (3)
C2	0.3568 (2)	0.03807 (8)	0.7242 (2)	3.88 (3)
C3	0.1789 (2)	0.07667 (9)	0.6942 (2)	4.74 (3)
C4	0.1736 (2)	0.1528 (1)	0.7720 (2)	5.20 (4)
C5	0.3423 (2)	0.1893 (1)	0.8773 (2)	5.44 (4)
C6	0.5194 (2)	0.1513 (1)	0.9074 (2)	4.92 (3)
C7	0.5267 (2)	0.07473 (8)	0.8297 (2)	3.88 (3)
C8	0.6991 (2)	0.02053 (9)	0.8412 (2)	4.15 (3)
C9	0.6090 (2)	−0.05352 (8)	0.7305 (2)	3.82 (3)
C10	0.6966 (2)	−0.12438 (9)	0.7019 (2)	4.33 (3)
C11	0.9062 (2)	−0.1414 (1)	0.7745 (2)	5.78 (4)

Table 2. Geometric parameters (\AA , $^\circ$)

O1—C1	1.257 (2)	C4—C5	1.383 (2)
O2—C10	1.334 (2)	C5—C6	1.380 (2)
C1—C2	1.469 (2)	C6—C7	1.385 (2)
C1—C9	1.434 (2)	C7—C8	1.509 (2)
C2—C3	1.390 (2)	C8—C9	1.503 (2)
C2—C7	1.391 (2)	C9—C10	1.359 (2)
C3—C4	1.376 (2)	C10—C11	1.481 (2)
O2—H2O	1.00 (2)		
C1—C9—C8	110.0 (1)	C10—O2—H2O	107 (1)
O2—C10—C11	114.8 (1)	C2—C1—C9	107.7 (1)
C7—C8—C9	102.56 (9)		
C1—C2—C7—C8	0.6 (2)	C1—C9—C10—O2	1.9 (2)
O1—C1—C9—C10	−2.4 (2)	C8—C9—C10—C11	−1.5 (2)

The crystal was sealed in a capillary to prevent sublimation. Programs used were *MolEN* (Fair, 1990) and *ORTEP* (Johnson, 1965).

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and geometry involving H atoms, complete geometry for non-H atoms and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71198 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1038]

References

- Cahn, R. S., Ingold, C. K. & Prelog, V. (1956). *Experientia*, 12, 81–94.
 Csöregi, I. & Norrestam, R. (1976). *Acta Cryst.* B32, 2450–2455.
 Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf-Nonius, Delft, The Netherlands.
 Forsén, S., Merényi, F. & Nilsson, M. (1964). *Acta Chem. Scand.* 18, 1208–1221.
 Garcia, J. G. & Enas, J. D. (1992). Unpublished results.

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Structure of 23,24-Dinor-5 α -cholan-12-one

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Abstract

The crystal and molecular structure of 23,24-dinor-5 α -cholan-12-one has been determined. Rings *A*, *B* and *C* have a chair conformation, ring *D* a half-chair conformation. All rings are *trans* connected. The crystal structure of the title compound confirms the link between a different kinetic behaviour during reduction of 12-oxosteroids with LiAlH_4 and a different orientation of the π system of the ketone functional group.

Comment

This paper forms part of a study on complex hydride reductions of 12-oxosteroids.

It has been reported that for LiAlH_4 the attack of a hydride is preferentially antiperiplanar with neighbouring axial protons (Biesemans, Van de Woude & van Hove, 1990). A conformation that makes such an antiperiplanar axial attack impossible would therefore show different kinetic properties towards complex hydride reduction.

Comparison of the kinetic data on C(17)-unsubstituted 12-oxosteroids and these C(17)-substituted ones reveals a diminished velocity of axial attack for the substituted steroids that cannot be explained on steric grounds. Therefore a change in conformation of the *C* ring on introduction of the C(17) substituent is suggested. NMR data confirm this observation in the solution state. To verify