Acta Cryst. (1989). C**45**, 659–661

Regiospecific Formation of a Methyl Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione-9-carboxylate Monoketal

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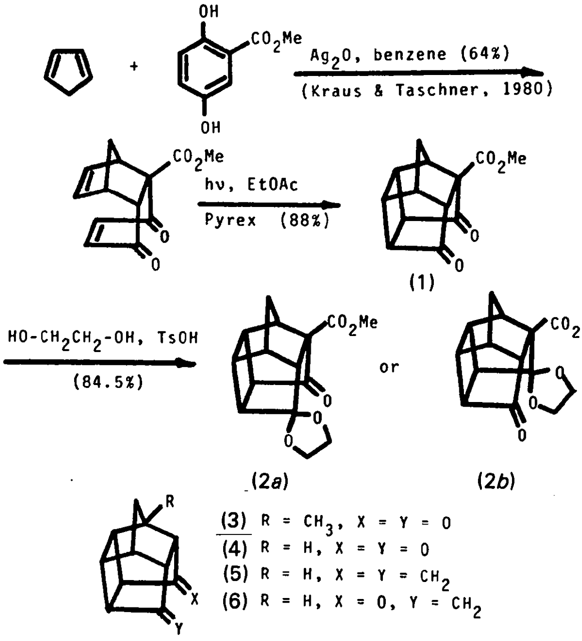
(*Received* 17 *June* 1988; *accepted* 31 *October* 1988)

Abstract. Methyl 11-ethylenedioxy-8-oxopentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-9-carboxylate, $C_{15}H_{16}O_5$, $M_r = 276\cdot29$, triclinic, $P\bar{1}$, $a = 6\cdot971\,(1)$, $b = 7\cdot488\,(1)$, $c = 13\cdot070\,(1)$ Å, $\alpha = 73\cdot90\,(1)$, $\beta = 79\cdot33\,(1)$, $\gamma = 78\cdot75\,(1)^\circ$, $V = 636\cdot7\,(1)$ Å^3, $Z = 2$, $D_x = 1\cdot441$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot71073$ Å, $\mu = 1\cdot01$ cm^{-1}, $F(000) = 292$, $T = 294$ K, $R = 0\cdot0379$ for 1450 reflections. The title compound is composed of a four-membered ring fused on three sides to three five-membered rings. The three five-membered rings are then fused to a fourth five-membered ring resulting in a norbornane moiety. The resulting structure may be described as a cage with one open end. In the parent diketone the two unconnected carbon atoms forming the open end are carbonyl moieties, and the carbon *p*-orbitals of these π-systems are collinear. In the title compound one of the ketones is replaced by a ketal functionality removing any potential *p*-orbital interactions. The two C—C distances one bond removed from the unconnected carbon atoms are the longest bonds in the title compound, 1·560 (2) and 1·577 (2) Å; however, they are significantly shorter than the calculated and observed distances in the parent diketone. This is consistent with a loss of coupling of the sp^2 carbon atoms in the parent diketone.

Introduction. As part of a program that involves the synthesis and chemistry of novel, substituted pentacyclo[5.4.0.0.^{2,6}.0^{3,10}.0^{5,9}]undecanes (Marchand, 1989), we recently synthesized methyl pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione-9-carboxylate (1) by using the route shown in Scheme 1. Subsequently, we observed that reaction of (1) with excess ethylene glycol in benzene in the presence of a catalytic amount of *p*-toluenesulfonic acid (Eaton, Cassar, Hudson & Hwang, 1976) afforded a single monoketal, m.p. 400–401 K, in 84·5% yield. Owing to the nonequivalence of the 8- and 11-ketone groups in (1), the monoketal thereby obtained can have either of two possible structures, (2*a*) or (2*b*) (Scheme 1). The question of the structure of this monoketal has been resolved *via* single-crystal X-ray structural analysis.



Scheme 1

Experimental. A transparent colorless crystal 0·30 × 0·35 × 0·35 mm; Nicolet *R*3*m*/*μ* update of a *P*2$_1$ diffractometer; data collected ($3 \leq 2\theta \leq 45^\circ$) in the ω-scan mode, scan rate 4 to 29·3° min^{-1} with scan range of 2° determined by peak profile plots, graphite-monochromated Mo *Kα* radiation; lattice parameters from a least-squares refinement of 25 centered reflections ($42\cdot06 \leq 2\theta \leq 48\cdot01^\circ$); no systematic absences, intensity statistics and Laue symmetry $\bar{1}$ from axial photographs consistent with space group $P\bar{1}$; monitored reflections (1$\bar{1}$6 and 443) showed only statistical variations in intensities; 1668 independent reflections

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Table 1. *Atomic coordinates* ($\times 10^4$) *and isotropic thermal parameters* (Å$^2 \times 10^3$)

	x	y	z	U*
C(1)	−40 (3)	7092 (3)	2275 (2)	49 (1)
C(2)	−1819 (3)	6067 (3)	2406 (2)	48 (1)
C(3)	−1183 (3)	4514 (3)	1797 (2)	47 (1)
C(4)	−1738 (3)	2771 (3)	2629 (2)	54 (1)
C(5)	−644 (3)	2983 (3)	3481 (1)	43 (1)
C(6)	−1448 (3)	5017 (3)	3570 (2)	47 (1)
C(7)	329 (3)	6044 (3)	3449 (2)	47 (1)
C(8)	2068 (3)	4500 (2)	3455 (1)	37 (1)
O(1)	3509 (2)	4235 (2)	3896 (1)	49 (1)
C(9)	1483 (2)	3197 (2)	2887 (1)	35 (1)
C(10)	1074 (3)	4301 (3)	1713 (1)	39 (1)
C(11)	1479 (3)	6297 (3)	1454 (1)	43 (1)
O(2)	3456 (2)	6409 (2)	1511 (1)	57 (1)
C(12)	4160 (4)	7723 (4)	598 (2)	75 (1)
C(13)	2542 (4)	8465 (4)	−39 (2)	86 (1)
O(3)	1123 (2)	7246 (2)	388 (1)	57 (1)
C(14)	2918 (3)	1404 (2)	2929 (1)	41 (1)
O(4)	3944 (2)	963 (2)	2170 (1)	68 (1)
O(5)	2955 (2)	357 (2)	3925 (1)	57 (1)
C(15)	4420 (3)	−1321 (3)	4078 (2)	66 (1)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Bond distances* (Å) *and valence angles* (°) *for compound* (2*a*)

C(1)—C(2)	1·542 (3)	C(1)—C(7)	1·560 (3)
C(1)—C(11)	1·522 (3)	C(2)—C(3)	1·537 (3)
C(2)—C(6)	1·550 (3)	C(3)—C(4)	1·513 (3)
C(3)—C(10)	1·536 (3)	C(4)—C(5)	1·519 (3)
C(5)—C(6)	1·545 (3)	C(5)—C(9)	1·557 (2)
C(6)—C(7)	1·544 (3)	C(7)—C(8)	1·503 (2)
C(8)—O(1)	1·205 (2)	C(8)—C(9)	1·529 (3)
C(9)—C(10)	1·577 (2)	C(9)—C(14)	1·504 (2)
C(10)—C(11)	1·509 (3)	C(11)—O(2)	1·414 (2)
C(11)—O(3)	1·420 (2)	O(2)—C(12)	1·398 (3)
C(12)—C(13)	1·456 (4)	C(13)—O(3)	1·410 (3)
C(14)—O(4)	1·196 (2)	C(14)—O(5)	1·323 (2)
O(5)—C(15)	1·448 (2)		
C(2)—C(1)—C(7)	90·3 (1)	C(2)—C(1)—C(11)	104·2 (2)
C(7)—C(1)—C(11)	111·5 (1)	C(1)—C(2)—C(3)	108·0 (1)
C(1)—C(2)—C(6)	89·8 (2)	C(3)—C(2)—C(6)	103·0 (1)
C(2)—C(3)—C(4)	103·4 (2)	C(2)—C(3)—C(10)	100·5 (2)
C(4)—C(3)—C(10)	104·8 (1)	C(3)—C(4)—C(5)	95·5 (2)
C(4)—C(5)—C(6)	103·1 (1)	C(4)—C(5)—C(9)	104·0 (1)
C(6)—C(5)—C(9)	101·1 (1)	C(2)—C(6)—C(5)	103·0 (2)
C(2)—C(6)—C(7)	90·6 (1)	C(5)—C(6)—C(7)	108·2 (1)
C(1)—C(7)—C(6)	89·3 (2)	C(1)—C(7)—C(8)	110·9 (2)
C(6)—C(7)—C(8)	103·3 (2)	C(7)—C(8)—O(1)	128·3 (2)
C(7)—C(8)—C(9)	104·1 (2)	O(1)—C(8)—C(9)	127·3 (2)
C(5)—C(9)—C(8)	100·9 (1)	C(5)—C(9)—C(10)	101·8 (1)
C(8)—C(9)—C(10)	110·3 (1)	C(5)—C(9)—C(14)	116·2 (1)
C(8)—C(9)—C(14)	113·0 (2)	C(10)—C(9)—C(14)	113·5 (1)
C(3)—C(10)—C(9)	103·1 (1)	C(3)—C(10)—C(11)	103·9 (1)
C(9)—C(10)—C(11)	111·2 (2)	C(1)—C(11)—C(10)	101·6 (1)
C(1)—C(11)—O(2)	114·4 (2)	C(10)—C(11)—O(2)	113·1 (1)
C(1)—C(11)—O(3)	111·2 (1)	C(10)—C(11)—O(3)	109·9 (2)
O(2)—C(11)—O(3)	106·7 (1)	C(11)—O(2)—C(12)	108·8 (2)
O(2)—C(12)—C(13)	106·8 (2)	C(12)—C(13)—O(3)	106·1 (2)
C(11)—O(3)—C(13)	106·9 (2)	C(9)—C(14)—O(4)	125·4 (1)
C(9)—C(14)—O(5)	111·6 (1)	O(4)—C(14)—O(5)	123·0 (2)
C(14)—O(5)—C(15)	116·6 (1)		

measured ($-7 \leq h \leq 7$, $7 \leq k \leq 8$, $0 \leq l \leq 14$), 1450 reflections $\geq 3\sigma(I)$; Lorentz–polarization corrections applied, ψ-scan-based absorption correction (transmission factors 0·822 to 0·851), structure solved by direct methods, block-cascade least-squares refinement, H atoms located in a difference map and refined isotropically; final $R = 0{\cdot}0379$, $wR = 0{\cdot}0470$ for 245 parameters and 1450 reflections ($R = 0{\cdot}0453$ and $wR = 0{\cdot}0549$ for all 1668 reflections $|F_o| > 0$), $S = 1{\cdot}572$, $(\Delta/\sigma)_{\max} = 0{\cdot}031$; largest peaks in the final difference map of $+0{\cdot}18$ and $-0{\cdot}17$ e Å^{-3}; $\sum w(|F_o| - |F_c|)^2$ minimized with $w = [\sigma^2(F_o) + 0{\cdot}00053F_o^2]^{-1}$. All computer programs supplied by Nicolet for Desktop 30 Microeclipse and Nova 4/C configuration (Nicolet Instrument Corporation, 1986); atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). Table 1 lists atomic positional parameters and Table 2 lists interatomic distances and valence angles, while Fig. 1 is a drawing of the title compound.*

Discussion. The reaction in Scheme 1 produces the open-cage structure (2*a*) which can be described as a fusion of four five-membered rings and one four-membered ring. The four-membered ring is planar (0·002 Å r.m.s.d.) with one side C(1)—C(7) [1·560 (2) Å] significantly longer than the other three sides which are statistically equivalent [1·542 (3) to 1·550 (3) Å]. The two five-membered rings containing C(4) adopt almost ideal envelope conformations while the other two five-membered rings are twisted. The ester side chain is in an extended planar (0·031 Å r.m.s.d.) conformation.

The general trends in bond lengths and angles are equivalent to those observed in the diketone (3)

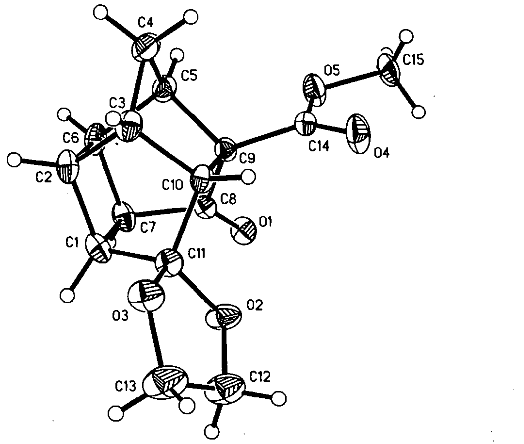

Fig. 1. Drawing of methyl 11-ethylenedioxy-8-oxopentacyclo-[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-9-carboxylate. Thermal ellipsoids are drawn at the 35% probability level. H atoms are represented by spheres of arbitrary size.

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* Lists of H-atom coordinates, anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51560 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(Marchand, Suri, Earlywine, Powell & van der Helm, 1984) and a series of monoketone complexes with an unsaturated six-membered-ring alcohol replacing one five-membered-ring ketone (Marchand, Annapurna, Watson & Nagl, 1989), except for the changes associated with the ketal functionality. While the C(1)—C(7) bond [1·560 (2) Å] and the C(9)—C(10) bond [1·572 (2) Å] are the longest bonds in compound (2*a*), they are significantly shorter than the corresponding bonds in diketone (3) and the related series of monoketone complexes. In the unsaturated compounds the π-orbitals on C(8) and C(11) are almost collinear and possibly overlap. The C(1)—C(7) and C(9)—C(10) bonds are parallel to these collinear π-orbitals and are one bond removed from C(8) and C(11). A STO-3G procedure was used to calculate the geometries of compounds (4)–(6) (Marchand, Huang, Kaya, Baker, Jemmis & Dixon, 1987) giving values of 1·572–1·575 and 1·579–1·585 Å for C(1)—C(7) and C(8)—C(9), respectively. Osawa & Kanematsu (1986) discussed various factors which might influence the bond lengths in open-cage structures such as (2). Through-space coupling involving direct interaction of the π-orbitals and through-bond coupling involving interaction of the π-orbitals with the parallel bonds were considered. STO-3G and photoelectron spectroscopy results were considered to be more consistent with through-bond coupling involving a 1,3 interaction pathway. Couplings by either mechanism might be expected to be absent in (2*a*) due to replacement of the π-bond at C(11) by a saturated ketal functionality. The C(1)—C(7) and C(9)—C(10) bonds in (2*a*) are significantly shorter than either those observed or calculated for the diketone; however, they remain the longest bonds in structure (2*a*). Molecular-mechanics calculations (Allinger & Yuh, 1980) do not take into account the π-orbital couplings and C(1)—C(7) and C(9)—C(10) bonds are calculated to be the same length in (2*a*) and (3), 1·522 and 1·555 Å, respectively. The decrease in bond lengths in going from (3) to (2*a*) appears to be related to the loss of coupling rather than to steric effects.

We thank the Welch Foundation (P-074 to WHW and B-963 to APM), the Air Force Office of Scientific Research and the Faculty Research Committees of Texas Christian University and the University of North Texas.

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Acta Cryst. (1989). C**45**, 661–663

Structure of a 3-Methylpentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione Monoethylene Ketal

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(*Received* 23 *September* 1988; *accepted* 1 *November* 1988)

Abstract. $C_{14}H_{16}O_3$, $M_r = 232·28$, triclinic, $P\bar{1}$, $a = 6·517$ (1), $b = 7·569$ (2), $c = 11·910$ (3) Å, $\alpha = 103·28$ (2), $\beta = 105·13$ (2), $\gamma = 91·71$ (2)°, $V = 549·5$ (2) Å^3, $Z = 2$, $D_x = 1·40$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 0·75$ mm^{-1}, $F(000) = 248$, $T = 295$ K, final $R = 0·042$, $wR = 0·044$ for 1419 observed

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