

### 193. Structure of a Tricyclic Photoproduct $C_{15}H_{24}O_3$ by X-Ray Analysis

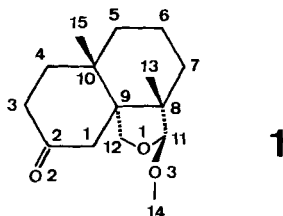
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*Summary.* The crystal structure of the photoproduct **1** ( $C_{15}H_{24}O_3$ ; monoclinic,  $a = 7.682$ ,  $b = 14.448$ ,  $c = 12.925 \text{ \AA}$ ,  $\beta = 108.4^\circ$ ; space group  $P2_1/c$ ,  $Z = 4$ ) has been determined by X-ray analysis. The structure was solved by direct methods and the positions of all hydrogen atoms were obtained from a difference synthesis. The final R factor is 0.049. The polycyclic skeleton of **1** consists of a *trans*-decalone ring system axially fused to an oxolane ring in a conformation intermediate between the envelope and twist form. Strong intramolecular non-bonded interactions are observed among the substituent atoms.

Irradiation of an  $\alpha,\beta$ -unsaturated  $\gamma$ -dimethoxy-methyl ketone afforded, in a  $\pi \rightarrow \pi^*$  induced process and in high yield, a mixture of epimeric products [1]. We here report the structure of one of the epimers (**1**) as determined by X-ray analysis<sup>1)</sup>.



**Experimental Part.** – The crystals were provided by M. J. Gloor (Dept. of Organic Chemistry, University of Geneva) and were colourless prisms with well formed faces. – Lattice parameters and diffracted intensities were measured at room temperature on an automatic four-circle Philips PW1100 diffractometer using graphite monochromator and  $MoK\alpha$ -radiation ( $\lambda = 0.7107 \text{ \AA}$ ). The selected crystal was sealed in a Lindemann capillary and had dimensions  $0.16 \times 0.19 \times 0.30 \text{ mm}$ . The crystallographic data are:

$$C_{15}H_{24}O_3 \text{ (m.p. } 126^\circ\text{). Monoclinic, space group } P2_1/c$$

$$a = 7.682 \text{ (3), } b = 14.448 \text{ (2), } c = 12.925 \text{ (2) \AA}$$

$$\beta = 108.4^\circ; U = 1361.2 \text{ \AA}^3; Z = 4$$

$$D_m = 1.232, D_x = 1.219 \text{ g cm}^{-3}; \mu = 0.71 \text{ cm}^{-1}$$

1276 reflections with  $\sin\theta/\lambda \leq 0.4813 \text{ \AA}^{-1}$  were scanned in the  $\theta - 2\theta$  mode (scan width  $1.2^\circ$ , scan speed  $0.02^\circ/s$ ). Three monitor reflexions were measured at average intervals of 30 reflections; no significant signs of crystal degradation were noticed. The usual corrections were applied, and a data set of 1029 structure amplitudes, with  $|F_o| > 2\sigma(F_o)$ , was obtained. No corrections were made for absorption.

**Structure Analysis and Refinement.** – The phase problem was solved by direct methods using the multiple solution procedure (MULTAN) [3]. The best results were obtained

<sup>1)</sup> A preliminary account of present results was given in [2].

with 170 of the largest normalized structure amplitudes ( $E > 1.54$ ) and 50 weaker values for the  $\psi_0$  test. The signs of three origin-determining reflections were fixed and those of three additional ones were varied to give eight starting sets of phases. The E-map based on the one with the highest 'figure of merit' revealed the locations of all the non-hydrogen atoms. Positional parameters and anisotropic temperature factors were then refined by full-matrix least-squares analysis. When the R-value was reduced to 0.10 all hydrogen atoms were unequivocally located from a difference synthesis and included in the structure model, but not refined. The condition for inclusion of a reflexion in a cycle of refinement was:

$$|F_o| \geq 3 \sigma(F_o); \text{ when } 2 \sigma(F_o) < |F_o| < 3 \sigma(F_o) \text{ only if } |F_c| > |F_o|.$$

The final R-value, based on 991 reflexions, was 0.049 with the weighting scheme:  $\omega = 1.0$  for  $|F| < 56$ ,  $\omega = 0.5$  for  $|F| \geq 56$ . The final atomic coordinates and thermal parameters are listed in Tables 1 and 2.

Table 1. Final positional and thermal parameters (both  $\times 10^4$ ) with standard deviations in parentheses. Thermal parameters are given in the form:  $\exp \{ -(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl) \}$

Atom	x	y	z	$b_{11}$	$b_{22}$	$b_{33}$	$b_{12}$	$b_{13}$	$b_{23}$
C(1)	-579(6)	2838(3)	1555(3)	151(10)	40(3)	60(4)	-10(9)	17(10)	-24(5)
C(2)	-2024(7)	3171(4)	540(4)	180(11)	80(4)	68(4)	-15(11)	24(12)	-56(7)
C(3)	-3004(7)	4053(4)	575(4)	199(12)	72(4)	66(4)	65(11)	11(11)	-7(6)
C(4)	-1788(6)	4801(3)	1305(4)	195(11)	51(3)	79(4)	52(9)	80(11)	29(6)
C(5)	603(7)	5197(3)	3077(4)	238(12)	41(3)	95(4)	-16(10)	77(12)	-37(6)
C(6)	1939(7)	4833(4)	4129(4)	229(12)	70(4)	90(5)	-66(11)	74(13)	-72(7)
C(7)	3275(6)	4134(3)	3853(3)	187(11)	60(3)	57(4)	-57(10)	21(10)	-24(5)
C(8)	2270(5)	3292(3)	3177(3)	139(9)	44(3)	50(3)	-22(8)	57(9)	4(5)
C(9)	666(5)	3632(3)	2168(3)	139(9)	33(2)	42(3)	-21(8)	57(9)	2(4)
C(10)	-564(5)	4408(3)	2409(3)	153(9)	34(2)	62(3)	-1(8)	73(10)	1(5)
C(11)	3619(6)	2888(3)	2659(4)	159(11)	47(3)	62(4)	-0(9)	64(10)	15(5)
C(12)	1793(6)	3967(3)	1429(3)	155(10)	59(3)	58(3)	22(9)	86(9)	22(5)
C(13)	1770(7)	2583(4)	3924(4)	243(12)	59(3)	63(4)	22(10)	103(11)	46(6)
C(14)	4698(7)	1532(4)	2051(4)	215(12)	65(4)	119(5)	78(10)	135(13)	-20(7)
C(15)	-1840(6)	4056(3)	3035(4)	188(11)	57(3)	75(4)	-7(9)	134(11)	-14(6)
O(1)	3458(4)	3437(2)	1721(2)	166(7)	74(2)	69(3)	16(7)	100(7)	31(4)
O(2)	-2414(6)	2694(4)	-275(4)	331(12)	163(5)	102(4)	155(11)	-121(10)	-160(7)
O(3)	3250(4)	1958(2)	2354(3)	167(7)	48(2)	104(3)	10(6)	93(8)	-12(4)

Table 2. Observed positional parameters of the hydrogen atoms ( $\times 10^4$ ). B is set equal to the isotropic thermal parameter of the carbon atom to which H is bonded

Atom	x	y	z	B(A <sup>2</sup> )	Atom	x	y	z	B(A <sup>2</sup> )
H(1)A	317	2262	1458	3.41	H(11)	5068	2799	3160	3.38
H(1)B	-1442	2517	2092	3.41	H(12)A	909	3823	546	3.38
H(3)A	-3715	4223	-248	4.70	H(12)B	2083	4765	1544	3.38
H(3)B	-4211	3796	864	4.70	H(13)A	996	1998	3508	4.06
H(4)A	-932	5078	827	4.22	H(13)B	2852	2260	4469	4.06
H(4)B	-2647	5363	1410	4.22	H(13)C	1219	2786	4502	4.06
H(5)A	1189	5628	2480	4.78	H(14)A	4864	1962	1350	5.14
H(5)B	-373	5714	3168	4.78	H(14)B	4608	819	1856	5.14
H(6)A	2942	5374	4550	5.27	H(14)C	5901	1517	2629	5.14
H(6)B	1157	4504	4634	5.27	H(15)A	-2642	3536	2686	3.86
H(7)A	4076	4453	3380	3.83	H(15)B	-2612	4635	3225	3.86
H(7)B	4150	3811	4635	3.83	H(15)C	-863	3851	3871	3.86

Table 3. *Molecular parameters derived from coordinates of Tables 1 and 2. For atom-numbering system, see I*

<i>Bond distances (Å). Standard deviations (<math>\times 10^3</math>) are in parentheses</i>			
C (1)–C (2)	1.505 (6)	C (8)–C (9)	1.564 (5)
C (1)–C (9)	1.543 (5)	C (8)–C (11)	1.520 (5)
C (2)–C (3)	1.501 (7)	C (8)–C (13)	1.536 (6)
C (2)–O (2)	1.214 (7)	C (9)–C (10)	1.560 (5)
C (3)–C (4)	1.531 (7)	C (9)–C (12)	1.554 (5)
C (4)–C (10)	1.547 (6)	C (10)–C (15)	1.542 (5)
C (5)–C (6)	1.535 (7)	C (11)–O (1)	1.417 (5)
C (5)–C (10)	1.536 (6)	C (11)–O (3)	1.403 (6)
C (6)–C (7)	1.525 (6)	C (12)–O (1)	1.435 (4)
C (7)–C (8)	1.554 (6)	C (14)–O (3)	1.430 (5)
<i>Bond angles (°). The average standard deviation is 0.36°</i>			
C (2)–C (1)–C (9)	112.1	C (7)–C (8)–C (13)	110.3
C (1)–C (2)–C (3)	119.2	C (9)–C (8)–C (11)	102.6
O (2)–C (2)–C (1)	119.2	C (9)–C (8)–C (13)	116.5
O (2)–C (2)–C (3)	121.6	C (11)–C (8)–C (13)	111.3
C (2)–C (3)–C (4)	113.7	C (8)–C (9)–C (1)	113.1
C (3)–C (4)–C (10)	112.8	C (8)–C (9)–C (10)	115.3
C (4)–C (10)–C (5)	108.8	C (8)–C (9)–C (12)	99.5
C (4)–C (10)–C (9)	108.1	C (1)–C (9)–C (10)	108.7
C (4)–C (10)–C (15)	107.7	C (1)–C (9)–C (12)	106.9
C (5)–C (10)–C (9)	111.3	C (10)–C (9)–C (12)	112.9
C (5)–C (10)–C (15)	107.8	O (1)–C (11)–C (8)	105.9
C (9)–C (10)–C (15)	113.1	O (1)–C (11)–O (3)	110.2
C (10)–C (5)–C (6)	111.3	C (8)–C (11)–O (3)	112.6
C (5)–C (6)–C (7)	109.9	O (1)–C (12)–C (9)	107.2
C (6)–C (7)–C (8)	114.1	C (11)–O (1)–C (12)	110.7
C (7)–C (8)–C (9)	110.1	C (11)–O (3)–C (14)	112.4
C (7)–C (8)–C (11)	105.2		
<i>Parameters involving H atoms: (Average values over the relevant groups present in the molecule)</i>			
– CH <sub>2</sub> –		– CH <sub>3</sub> –	
C–H	1.13 (4) Å	C–H	1.06 (6) Å
H–C–H	107 (6)°	H–C–H	105 (6)°
X–C–H	110 (5)°	X–C–H	113 (5)°

**Discussion of the results.** – The molecular parameters are given in Table 3. Although all H atoms were well resolved and spherical, only average geometries are reported for the methylene and methyl groups. Stereoscopic views of the molecular conformation and packing are given in Fig. 1 and 2.

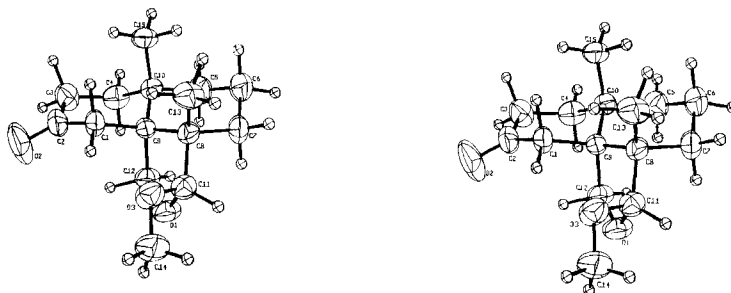


Fig. 1. Stereoscopic view of the molecular conformation

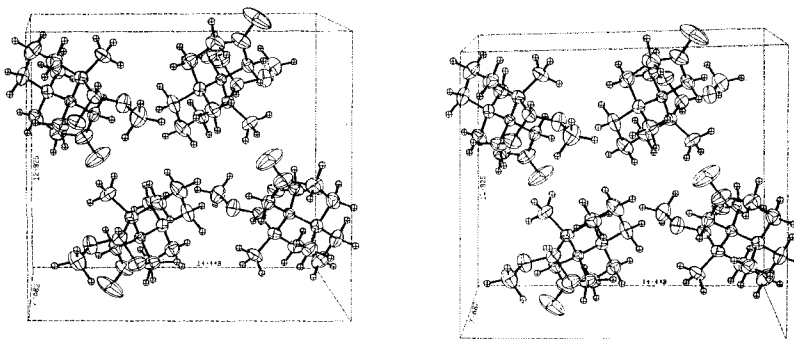


Fig. 2. Stereoscopic view of the molecular packing within the unit cell. The origin and the basic molecule ( $x, y, z$ ) are in the rear, upper left corner

The rigid decalone system assumes an all-chair conformation. Atoms C(1), C(2), C(3), O(2) are coplanar (mean deviation 0.007 Å); the central atom is  $sp^2$  hybridized as shown by the bond angles close to  $120^\circ$  at C(2). The C(2)–O(2) bond almost eclipses the adjacent C–H bonds, with torsion angles  $\tau[\text{H}(1)\text{A}-\text{C}(1)-\text{C}(2)-\text{O}(2)] = 15.3^\circ$  and  $\tau[\text{H}(3)\text{A}-\text{C}(3)-\text{C}(2)-\text{O}(2)] = -14.7^\circ$ . The O(2) atom is 2.43 and 2.62 Å from atoms H(3)A and H(1)A, respectively.

The *trans*-decalone system is distorted as expressed by the torsion angles (Fig. 3A) which deviate from the normal values expected for an unstrained molecule<sup>2)</sup>. The strain is caused by fusion to the oxolane ring and by strong steric repulsion between the axial methyl groups, which are splayed apart; the bonds C(8)–C(13) and C(10)–C(15) diverge by as much as  $29.2^\circ$ . Additional indications for such a repulsion are the long bonds (av. 1.562 Å) between the bridgehead atoms as compared to the other  $C(sp^3)-C(sp^3)$  bonds (av. 1.539(10) Å) of the decalone system. The H atoms of

<sup>2)</sup> Torsional angles of some fused non-aromatic ring systems are discussed in [4].

the methyl groups are forced into close contact with those of the methylene groups at C(1), C(5) and C(6): the shortest distance 1.82 Å is observed between H(15)C and H(6)B.

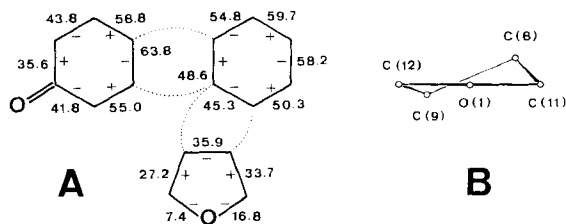


Fig. 3. A) Exploded view of the polycyclic skeleton showing the torsion angles ( $^{\circ}$ ) in the component rings. B) Projection of the oxolane ring onto a plane perpendicular to the plane C(11)–O(1)–C(12)

The oxolane ring looks intermediate between envelope and twist form with  $C_2$  passing through O(1) (Fig. 3B). The distance between H(12)B of the oxolane ring and H(5)A of the B-ring is only 2.00 Å. Atoms C(14)–O(3) of the methoxy group tend to assume the favoured planar (T.T.T...) conformation together with atoms C(11)–C(8) of the five-membered ring (mean deviation 0.064(2) Å). The oxygen O(3) is forced into close contact with the neighbouring  $-\text{CH}_2$  group of the A-ring; the H(1)A...O(3) separation (2.23 Å) is about 0.4 Å smaller than the sum of *van der Waals* radii. Other relevant non-bonded distances and angles are: C(1)...O(3) = 3.069 Å; O(3)...C(1)–H(1)A = 33.5°; C(14)–O(3)...H(1)A = 133.5°;  $\tau[\text{H}(1)\text{A} \dots \text{O}(3)\text{--C}(14)\text{--H}(14)\text{C}] = 177.4^{\circ}$ . One of the  $\text{sp}^3$  lone pair orbitals of O(3) thus points towards H(1)A, suggestive of a specific C–H...O bonding interaction, as proposed by other workers [5].

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#### BIBLIOGRAPHY

- [1] *J. Gloor & K. Schaffner*, *Helv.* 57, 1815 (1974).
- [2] *J. Gloor, G. Bernardinelli, R. Gerdil & K. Schaffner*, *Helv.* 56, 2520 (1973).
- [3] *G. Germain, P. Main & M. M. Woolfson*, *Acta Crystallogr.* A27, 368 (1971).
- [4] *H. J. Geise, C. Altona & C. Romers*, *Tetrahedron* 23, 439 (1967); *ibid.* 24, 13 (1968).
- [5] a) *J. Gaultier & C. Hauw*, *Acta Crystallogr.* 21, 694 (1966) and references therein; b) *G. Bernardinelli & R. Gerdil*, *Helv.* 57, 1459 (1974).