Crystal Structure of 2-Hydroxy-1,3,4,6,8,9-hexamethyltricyclo[4.4.0.0^{2,8}]-deca-3,9-dien-5-one †

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Crystals of the title compound (II) are triclinic, a = 7·832(1), b = 13·797(3), c = 6·731(1) Å, α = 98·21(3), β = 101·36(2), γ = 92·71(3)°, Z = 2, space group $P\bar{1}$. The structure was determined from diffractometer data by direct methods, and refined by full-matrix least-squares techniques to R 0·061 for 1774 observed reflections. One six-membered ring has a half-chair and the other a boat conformation, the latter as part of a norbornene system. Some of the bonds are longer than normal.

PHOTOLYSIS of Diels–Alder adducts of *p*-benzoquinone has been a productive means of synthesis of novel sesquiterpene-like tricyclic ring systems.[1-3] Irradiation of the substituted butadiene–*p*-benzoquinone Diels–Alder adduct (I) gave two products.[4] Spectroscopic evidence could not distinguish between the two possible structures (II) and (III) for one of these, and a single-crystal analysis was undertaken to establish its identity.

EXPERIMENTAL

Crystals of the compound are white needles, the a axis being coincident with the needle axis. Unit-cell and space-group data were determined from film and diffractometer measurements.

Crystal Data.—$C_{16}H_{22}O_2$, M = 246·35. Triclinic, a = 7·832(1), b = 13·797(3), c = 6·731(1) Å, α = 98·21(3), β =

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† The name provided in the title for this compound is based on systematic numbering, and is to be preferred. However, throughout the rest of the paper the compound is named as 5-hydroxy-1,3,4,6,8,9-hexamethyltricyclo[4.4.0.0^{5,9}]deca-3,7-dien-2-one, and all atomic numbers are derived from the numbering indicated in this name (see Figure 1).

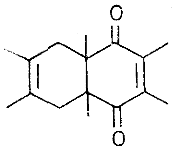
[1] J. R. Scheffer, J. Trotter, R. A. Wostradowski, C. S. Gibbons, and K. S. Bhandari, *J. Amer. Chem. Soc.*, 1971, **93**, 3813.

[2] J. R. Scheffer, K. S. Bhandari, R. E. Gayler, and R. H. Wiekenkamp, *J. Amer. Chem. Soc.*, 1972, **94**, 285.

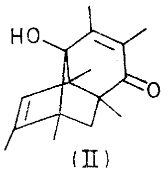
[3] J. R. Scheffer and R. A. Wostradowski, *Tetrahedron Letters*, 1972, 677.

[4] J. R. Scheffer, J. Trotter, R. E. Gayler, and C. A. Bear, *J. Amer. Chem. Soc.*, in the press.

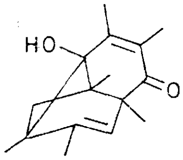
101·36(2), γ = 92·71(3)°, U = 703·6(3) Å^3, Z = 2, D_c = 1·16. Cu-K_α radiation, λ = 1·5418 Å; μ(Cu-K_α) = 5·94 cm^{-1}. Space group $P\bar{1}$ (No 2).



(I)



(II)



(III)

The intensities of the reflections were measured on a Datex-automated General Electric XRD 6 diffractometer with Cu-K_α radiation. With $2\theta \leqslant 120°$, 2071 reflections were measured of which 1774 (85·7%) were considered observed, having $I > 3\sigma(I)$, where $\sigma(I)$ is defined by $\sigma^2(I) = S + B + (0{\cdot}05S)^2$, S is the scan count, and B the background count. Lorentz and polarisation factors were applied but no absorption corrections were made.

TABLE 1

Final positional parameters (fractional × 10^4) of the carbon and oxygen atoms

	x	y	z
C(1)	1445(3)	3163(2)	2309(3)
C(2)	−110(3)	2615(2)	809(4)
C(3)	251(3)	1771(2)	−598(4)
C(4)	1922(3)	1628(2)	−711(3)
C(5)	3407(3)	2347(2)	519(3)
C(6)	2884(3)	3404(2)	1067(3)
C(7)	4493(3)	3832(2)	2639(4)
C(8)	5168(3)	3144(2)	3645(4)
C(9)	4005(3)	2198(2)	2805(3)
C(10)	2314(3)	2403(2)	3612(4)
C(11)	920(4)	4055(2)	3566(5)
O(12)	−1595(2)	2849(2)	816(3)
C(13)	−1290(4)	1100(3)	−1806(6)
C(14)	2399(4)	763(2)	−2055(6)
O(15)	4751(2)	2287(1)	−614(3)
C(16)	2319(4)	3983(2)	−666(5)
C(17)	6646(4)	3226(2)	5451(5)
C(18)	4790(4)	1249(2)	3200(5)

Carbon and oxygen atom anisotropic thermal parameters, and hydrogen atom positional and isotropic thermal parameters have been deposited with the structure-factor Table in Supplementary Publication No. SUP 20860.

Structure Analysis.—The structure was solved by the symbolic addition procedure, using the SAP programs of Ahmed and Hall.[5] The structure was refined by full-matrix least-squares methods. The function minimised was $\Sigma w(F_o - F_c)^2$, where $w = 4I/\sigma^2(I)$. The carbon and oxygen atoms were refined, first with isotropic and then anisotropic thermal parameters. Hydrogen atoms were located from a difference-Fourier synthesis and refinement continued with the hydrogen atoms included and being refined with isotropic temperature factors. For the 1774 observed reflections the final R was 0·061 and R' 0·080. Measured and calculated structure factors are listed in Supplementary Publication No. SUP 20860 (21 pp., 1 microfiche).* Positional and thermal parameters are given in Table 1, and bond lengths are listed in Table 2.

TABLE 2

Bond distance (Å) and angles (deg.)

C(1)–C(2)	1·512(3)	C(5)–C(6)	1·547(3)
C(1)–C(6)	1·580(3)	C(5)–C(9)	1·563(3)
C(1)–C(10)	1·558(3)	C(5)–O(15)	1·416(3)
C(1)–C(11)	1·513(3)	C(6)–C(7)	1·511(3)
C(2)–C(3)	1·468(3)	C(6)–C(16)	1·514(3)
C(2)–O(12)	1·222(3)	C(7)–C(8)	1·315(3)
C(3)–C(4)	1·348(3)	C(8)–C(9)	1·525(3)
C(3)–C(13)	1·506(3)	C(8)–C(17)	1·492(3)
C(4)–C(5)	1·516(3)	C(9)–C(10)	1·551(3)
C(4)–C(14)	1·500(4)	C(9)–C(18)	1·508(3)

Angles at carbon: 94·3—129·6(2)°. Distances and angles involving hydrogen atoms are listed in Supplementary Publication No. SUP 20860.

DISCUSSION

The analysis has shown that this particular photoproduct is obtained from the Diels–Alder adduct (I) by the formation of the C(5)–C(9) bond (see Figure 1) and thus formula (II) is correct.

With the formation of the C(5)–C(9) bond a norbornene system has been produced from C(1) and C(5)–C(10). The six-membered ring, C(1), C(6)—(10), has a distorted boat conformation (see Table 3) in which the C(6) to C(9) distance (2·28 Å) is significantly shorter than the calculated value (2·57 Å) for an ideal boat form. The angle at the apex of the bridge is 94·3° and, as such, is in agreement with other compounds [6-10] featuring a norbornane skeleton where this value ranges from 92·5 to 94·4°. Three of the bonds in this part of the molecule are longer than normal, *i.e.*, C(1)–C(6) 1·580, C(5)–C(9) 1·563, and C(1)–C(10) 1·558 Å, and this may be attributed to strain in the norbornane skeleton. With respect to the lengthening of the C(1)–C(6) bond, in compounds [9,10] with a saturated norbornane system the

TABLE 3

Equations of mean planes and deviations (Å) of relevant atoms from the planes *

Plane (1): C(1), C(7), C(8), C(10)

$$0{\cdot}245X - 0{\cdot}468Y - 0{\cdot}849Z + 3{\cdot}069 = 0$$

C(1) 0·015, C(7) −0·021, C(8), 0·021, C(10) −0·018, C(5) 1·892, C(6) 0·800, C(9) 0·876

Plane (2): C(2)—(5)

$$0{\cdot}035X + 0{\cdot}669Y - 0{\cdot}743Z - 1{\cdot}957 = 0$$

C(2) −0·006, C(3) 0·013, C(4) −0·011, C(5) 0·005, C(1) −0·296, C(6) 0·658

* X, Y, and Z in Å with respect to orthogonal axes a, b' and c^*.

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* For details of Supplementary Publications see Notice to Authors No. 7, in *J.C.S. Perkin II*, 1972, Index Issue.

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[6] R. Destro, G. Filippini, C. M. Gramaciolo, and M. Simonetta, *Tetrahedron Letters*, 1968, 5955; 1969, 3223.

[7] A. C. MacDonald and J. Trotter, *Acta Cryst.*, 1965, **18**, 243.

[8] A. C. MacDonald and J. Trotter, *Acta Cryst.*, 1965, **19**, 456.

[9] Y. Morino, K. Kuchitsu, and A. Yokozeki, *Bull. Chem. Soc. Japan*, 1967, **40**, 1552.

[10] C. S. Gibbons and J. Trotter, *J.C.S. Perkin II*, 1972, 737.

analogous bond is not lengthened but it is, however, in those compounds[6,7] with a double bond. Thus this particular long bond is possibly due to the steric requirements resulting from the introduction of the double bond. The angles, though significantly less than normal, are in agreement with those found in other compounds containing a norbornane skeleton.[6-10]

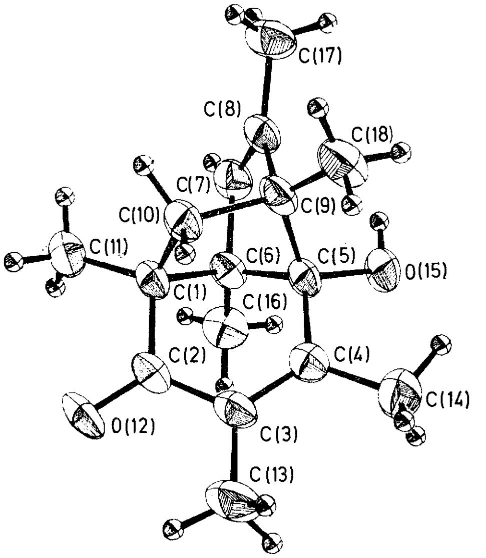

FIGURE 1 The structure showing the atom numbering system

The other six-membered ring, C(1)—(6), is in the half chair conformation with atoms C(2)—(5) approximately planar while C(1) and C(6) are displaced on opposite sides of the mean plane by 0·30 and 0·66 Å respectively. There is some conjugation evident in this ring with C(2)–C(3) shorter than normal (1·468 Å).

Other bond lengths agree reasonably well with expected values except that C–C(Me) lengths are shorter than normal, but this is possibly due to thermal libration.

There is hydrogen bonding between the hydrogen of the hydroxy-group and the carbonyl oxygen of the molecule related by $1 + x,y,z$ (O · · · H 2·145 Å). All other contacts are normal van der Waals distances and Figure 2 shows the packing of the molecules in the unit cell as well as the hydrogen bond.

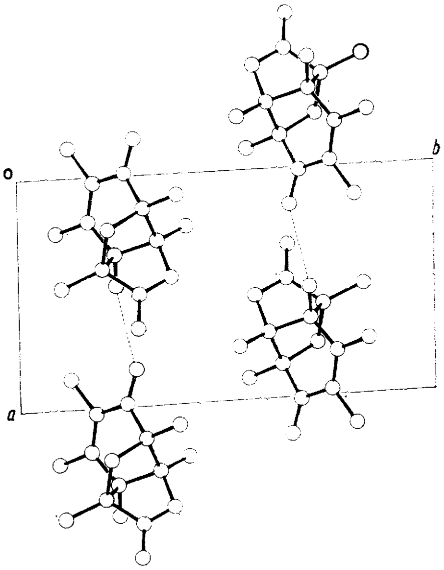

FIGURE 2 Projection of the unit cell along c^*. Dotted lines show hydrogen bond

We thank Dr. J. R. Scheffer for the crystals and discussion, and the National Research Council of Canada for financial support.

[3/579 *Received*, 29*th March*, 1973]