September, 1982] © *1982 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn., 55, 3041—3042 (1982)* 3041

X-Ray Crystallographic Analysis of 3α,5-Epoxy-6β-iodo-3β-methyl-*A*-homo-4-oxa-5α-cholestane, a Major Product of Photo- and Thermally-induced Radical Rearrangements of Hypoiodites of 3α- and 3β-Methyl-5-cholesten-3-ols[1)]

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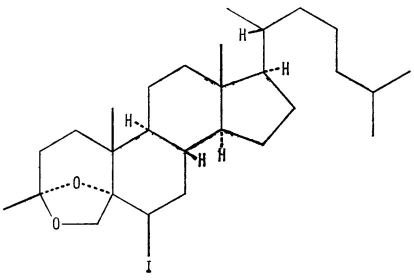
(Received December 5, 1981)

Synopsis. The major product of photo- and thermally-induced radical rearrangements of hypoiodites of 3α- and 3β-methyl-5-cholesten-3-ols in the presence of iodine with mercury(II) or silver(II) oxide has been established as 3α,5-epoxy-6β-iodo-3β-methyl-*A*-homo-4-oxa-5α-cholestane by means of X-ray crystal structure analysis.

The photo- and thermally-induced rearrangements of hypoiodites of several 5-cholesten-3-ols in the presence of mercury(II) oxide and iodine generally lead to the formation of seven-membered oxabicyclics.[2–5)] In a previous paper,[3)] it was reported that hypoiodites of 3α- and 3β-methyl-5-cholesten-3-ols in benzene containing mercury(II) oxide and iodine gave virtually a single product. The **1** structure was proposed for this product on the basis of the spectroscopic data.[3)] There was, however, some ambiguity in assigning the stereochemistry of its oxygen bridge. Therefore, in order to establish **1**, we have now undertaken an X-ray crystal structure analysis.



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Experimental

A colorless single crystal with dimensions of about 0.2×0.2×0.5 mm³ was used for the X-ray measurement. The crystal data are as follows: $C_{28}H_{47}O_2I$, mol wt 542.6, orthorhombic, space group $P2_12_12_1$, $a=17.44(1)$, $b=21.27(2)$, $c=7.26(1)$ Å, $Z=4$, $D_c=1.338$ g cm^{-3}, μ(Mo $K\alpha$)$=11.9$ cm^{-1}. The cell dimensions and diffraction intensities were measured at about −80 °C on a Hilger & Watts four-circle diffractometer with Zr-filtered Mo $K\alpha$ radiation (λ=0.71069 Å). The ω-2θ step-scan technique was applied at an ω interval of 0.02°; the counting time at each step was 1 s. The background was measured for 25 s at each end of the scan range. The intensities thus obtained were corrected for the Lorentz and polarization factors, but not for the absorption or the extinction effect. In the range of 2θ values up to 48°, 1786 independent structure-factor amplitudes above the 3$\sigma(F)$ level were selected for the structure determination.

Structure Determination

The structure was solved by the Monte Carlo direct method,[6)] using the 20 strongest reflections as a starting set. In order to extend the tentative-phase set derived from random numbers, 12 cycles of the tangent procedure were carried out using 489 $|E|$ values above 1.30. Since the first random-phase set gave a low R_K value of 0.142 ($R_K=\Sigma||E_o|-k|E_c||/\Sigma|E_o|$), 6 additional cycles of the tangent procedure were performed by the use of 761 $|E|$ values above 1.10. An *E*-map based on 757 phases afforded all the 31 non-hydrogen atoms. The structure thus obtained was refined by the block-diagonal least-squares method with

Table 1. The final atomic parameters and estimated standard deviations

Atom	$x(\times 10^4)$	$y(\times 10^4)$	$z(\times 10^3)$	B_{eq}[a)]/Å²
I	4069.8(6)	3637.0(5)	130.6(2)	4.61
O(1)	1994(5)	4951(3)	−86(1)	3.34
O(2)	1658(4)	4067(3)	59(1)	2.54
C(1)	1834(8)	3889(5)	−318(2)	3.42
C(2)	1141(7)	4219(6)	−233(2)	3.25
C(3)	1349(7)	4547(5)	−56(2)	2.95
C(4)	2712(7)	4617(5)	−51(2)	3.81
C(5)	2434(7)	3936(6)	−9(2)	2.92
C(6)	2840(6)	3629(6)	157(2)	2.93
C(7)	2522(7)	2965(6)	199(2)	3.40
C(8)	2421(7)	2548(6)	27(2)	2.69
C(9)	2008(7)	2870(5)	−125(2)	2.64
C(10)	2390(7)	3499(5)	−188(2)	2.99
C(11)	1896(7)	2415(5)	−294(2)	2.87
C(12)	1486(8)	1805(6)	−235(2)	3.04
C(13)	1897(6)	1473(5)	−71(2)	2.45
C(14)	1994(6)	1957(5)	84(2)	2.34
C(15)	2268(8)	1568(6)	245(2)	3.53
C(16)	1797(7)	923(6)	221(2)	3.28
C(17)	1439(6)	935(5)	28(2)	1.99
C(18)	2723(6)	1194(5)	−136(2)	3.28
C(19)	3141(7)	3395(6)	−289(2)	3.36
C(20)	1406(7)	269(5)	−58(2)	2.67
C(21)	1143(8)	291(6)	−262(2)	3.43
C(22)	901(9)	−126(5)	57(2)	2.82
C(23)	875(8)	−845(5)	5(2)	2.78
C(24)	390(6)	−1224(5)	140(2)	3.70
C(25)	442(7)	−1954(5)	106(3)	4.70
C(26)	219(9)	−2160(6)	−75(2)	5.97
C(27)	−35(9)	−2257(7)	261(3)	7.51
C(28)	740(8)	4889(6)	39(2)	4.39

a) $B_{eq}=8\pi^2(u_1^2+u_2^2+u_3^2)/3$, where u_i is the root-mean-square deviation in the *i*-th principal axis of the thermal ellipsoid.

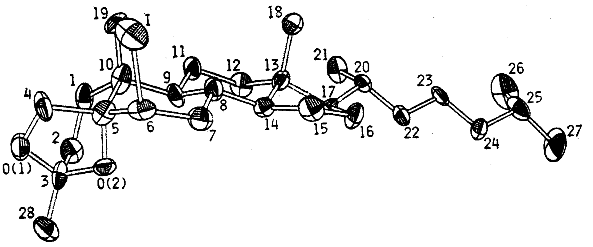

Fig. 1. A perspective view of the 3α,5-epoxy-6β-iodo-3β-methyl-*A*-homo-4-oxa-5α-cholestane molecule, and the numbering system of atoms.
Non-hydrogen atoms are represented as thermal ellipsoids enclosing 50% probabilities.

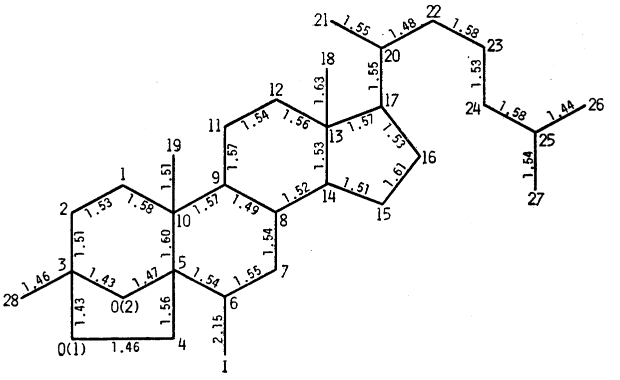

Fig. 2. The bond distances (*l*/Å).
The e.s.d.'s are 0.02—0.03 Å for C–C, 0.01—0.02 Å for C–O, and 0.01 Å for C–I.

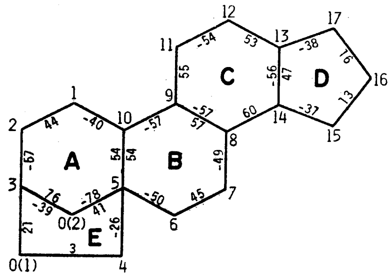

Fig. 3. The torsion angles (*ϕ*/°).
Only the torsion angles relevant to atoms which form the same ring are given in the ring.

anisotropic temperature factors. After 29 hydrogen atoms had been located in a difference Fourier map, further least-squares refinements were repeated including the hydrogen atoms with isotropic temperature factors. Since the absolute configuration of the present molecule was known,$^{3)}$ the anomalous dispersion effects of the iodine atoms were included in these last refinements. The weighting scheme used was as follows:

$$w = 1/\{\sigma(F)^2 \exp(AX^2+BY^2+CXY+DX+EY)\},$$

where $X=|F_o|$ and $Y=\sin\theta/\lambda$. The A, B, C, D, and E coefficients are constants which were evaluated from the $(\Delta F)^2$ distribution in the (X,Y) space; $A=-0.1136\times10^{-5}$, $B=12.40$, $C=0.04025$, $D=-0.008957$, and $E=-12.24$. The final R value was 0.064. The final atomic parameters are listed in Table 1.$^{7)}$

The calculations were performed on a HITAC M-200H computer at the Hokkaido University Computing Center, using our own programs. The atomic scattering factors were taken from the International Tables.$^{8)}$

Results and Discussion

The molecular framework is shown in Fig. 1. It is concluded that the major product of the rearrangements of hypoiodites of 3α- and 3β-methyl-5-cholesten-3-ols has the **1** structure. The bond distances and torsion angles are given in Figs. 2 and 3, respectively. The A/B ring junction is cis. All the six-membered A-, B-, and C-rings take chair conformations, while the five-membered D- and E-rings adopt half-chair and envelope conformations respectively. The chair conformation of the A-ring is remarkably deformed by the bridging of the C(4)H_2–O(1) group so that the puckering of the C(3)–O(2)–C(5) part is great, whereas that of the C(2)–C(1)–C(10) part is small. Because of the occupation of the 1,3-diaxial positions on the B-ring, the C(19) and I atoms approach each other at a considerably shorter distance (3.49(1) Å) than the sum of their van der Waals radii, 4.15 Å. This severe steric hindrance results in an enlargement of the C(5)–C(10)–C(19) and C(9)–C(10)–C(19) bond angles (116(1) and 113(1)° respectively) and a closing of the C(5)–C(6)–C(7)–C(8) torsion angle (45°). As Fig. 1 shows, the C(20)–C(22)–C(23)–C(24)–C(25)–C(27) side chain, together with the C(13) and C(17) ring atoms, takes a nearly-planar zigzag conformation.

We thank Professor Jiro Tanaka of Nagoya University for the generous permission to use a four-circle diffractometer.

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