imer.

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Registry No.—**1**, 32897-40-8; **2**, 68875-92-3; **3**, 52392-70-8; **4**, 68907-09-5; **5**, 29654-59-9; **6**, 68875-93-4; **7a**, 1636-25-5; **7b**, 4371-02-2; **8a**, 7782-29-8; **8b**, 2328-24-7; **9**, 63520-69-4; **10**, 63520-66-1; **11**, 68907-10-8; ChNB, 23838-12-2; cholesterol, 57-88-5.

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Notes

X-ray Crystal and Molecular Structure of a Bridgehead Diene

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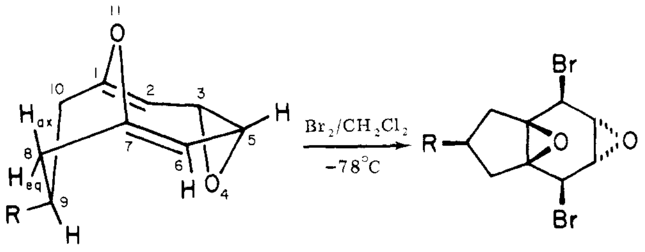
Recently we reported[1] the synthesis of the strained bridgehead diene **1a** (Scheme I) and the characterization of its transannular bromination product **2a** by X-ray crystal analysis. Examination of a molecular model of the oxepin oxide **1a** reveals considerable distortion of the bridgehead double bonds, but disappointingly the crystals of **1a** are not suitable for X-ray crystal analysis. Herein we report the synthesis, characterization, and X-ray crystal structure of derivative **1b** ((*ps*,3*R*,5*S*,9*s*)-9-methoxy-4,11-dioxatricyclo-[5.3.1.0^{3,5}]undeca-1,6-diene) and its transannular bromination to **2b**.

The synthesis of oxepin oxide **1b** from *syn*-2-hydroxyindane 3a,7a-oxide[2] follows the route previously reported[1] for the unsubstituted diene **1a**. The chemical consequences of locking the oxepin oxides **1a** and **1b** into the pictured transoid[3] conformations have been discussed.[1]

Scheme I



1a, R = H
1b, R = OCH_3

2a, R = H
2b, R = OCH_3

Results and Discussion

An X-ray crystal analysis of oxepin oxide **1b** yields the perspective view of the molecule shown in Figure 1. In the crystal, the six-membered ring (C_1, C_{7-10}, and O_{11}) adopts a distorted chair conformation in which the bridgehead atoms C_1 and C_7 are held close together (distance C_1–C_7 = 2.176 (0.004)[4] Å; compare C_8–C_{10} = 2.564 (0.004)[4] Å). The methyl ether oxygen (O_{12}) assumes an equatorial position and the methyl group (C_{13}) takes a noneclipsed position between C_{10} and H_9 (dihedral angle C_{10}–C_9–O_{12}–C_{13} = 67.2° (0.3°)[4]).

The bridgehead double bonds display virtually identical

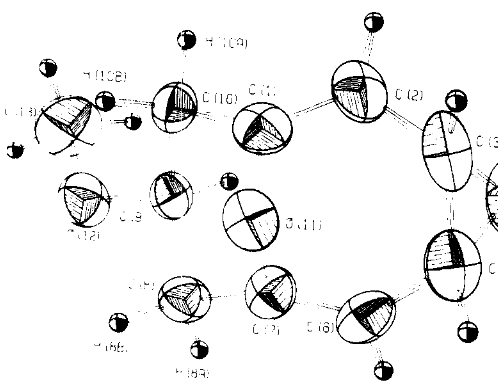


Figure 1. Perspective view of oxepin oxide **1b**.

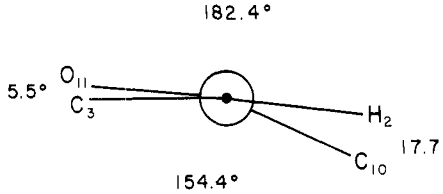


Figure 2. A projection of the bridgehead double bond viewed down the C_2–C_1 bond. The standard deviations for the angles are: 154.4° (0.3°), 5.5° (0.4°), 182.4° (1.8°), and 17.7° (1.8°).

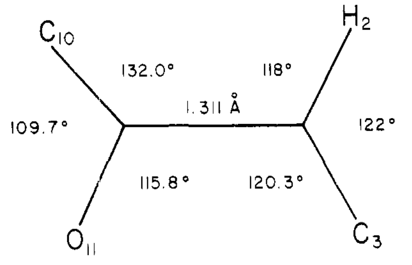


Figure 3. The C_1–C_2 double bond viewed from above the twisted π system. The standard deviations for the data reported are: 1.311 Å (0.004 Å), 118° (1°), 122° (2°), 120.3° (0.3°), 115.8° (0.3°), 109.7° (0.2°), 132.0° (0.3°).

geometries; their distortion can be appreciated readily in the projections of the C_1–C_2 double bond shown in Figures 2 and 3. The double bonds are twisted (Figure 2) and the carbons, especially the bridgehead carbons, are pyramidalized (distance from C_1 to plane of C_2, C_{10}, O_{11} = 0.13 Å). From the angles in Figure 2 it is calculated that the dihedral angle between the axes of the π orbitals at C_1 and C_2 is 11.6°. The slight pyramidalization at C_2 (distance from C_2 to plane of H_2, C_1, C_3 = 0.05 Å) tips the C_2 π orbital toward the C_1 π orbital; this effect has been treated theoretically[5] and is observed in other molecules.[6,7] The C_1–C_2 bond distance (1.311 Å) is normal for a carbon–carbon double bond (compare ethylene, C–C distance = 1.332 Å),[8] yet Figure 3 shows significant differences in bond angles at C_1 and C_2. Although the bond angles at C_2 are unexceptional, the geometrical constraints at the bridgehead (C_1) open the C_2, C_1, C_{10} angle to 132.0° and close the C_{10}, C_1, O_{11} and O_{11}, C_1, C_2 angles to 109.7 and 115.8°, respectively.

It is straightforward to calculate the Slater-AO overlap integral for the C_1–C_2 double bond by the method of Mulliken et al.[9] Assuming that the π orbitals at C_1 and C_2 are pure p orbitals[10] the overlap is calculated by decomposing the orbitals into components along (σ) and perpendicular to (two orthogonal π components) the C_1–C_2 axis. The total calculated overlap ($S_{1,2}$ = 0.277) lies in the normal range for a carbon–carbon double bond (the 1,2-overlap in *trans*-1,3-butadiene,[11] $S_{1,2}$ = 0.278, and the three double bond overlaps in an ester of the cycloheptatriene, thujic acid,[11] $S_{1,2}$ = 0.266, $S_{3,4}$ = 0.272, and $S_{5,6}$ = 0.275).

Table I. Angles between Selected Hydrogen Atoms and the Corresponding $^1H/^1H$ Coupling Constants

atoms	dihedral or bond angles, deg[a]	measured $^1H/^1H$ coupling constant, Hz
H_5-C_5-C_6-H_6	69.9 (2.4)	1.6 ± 0.2[b]
H_9-C_9-C_8-H_8^{ax}	168.1 (2.0)[c]	9.8
H_9-C_9-C_8-H_8^{eq}	50.1 (2.1)[c]	5.5
H_8^{ax}-C_8-H_8^{eq}	109 (2)	11.5

[a] Figures presented in parentheses are standard deviations. [b] From analysis of the AA'XX' half spectrum of H_3 and H_5. [c] The conformation of the six-membered ring is not locked; however, the chair conformation seen in the crystal should predominate in solution.

Appreciable interaction between the bridgehead π orbitals is suggested by the transannular mode of bromination of **1b** (and **1a**). Thus, titration of a CH_2Cl_2 solution of **1b** with Br_2/CH_2Cl_2 at −78 °C yields the dibromo diepoxide **2b** (71%). The Slater-AO overlap integral between the C_1 and C_7 π orbitals, calculated assuming the C_1 and C_7 π orbitals are pure p orbitals,[10] is large ($S_{1,7}$ = 0.124). In the transition state for bromination (**1b** → **2b**) this assumption may be geometrically accurate as the conversion **1b** → **2b** proceeds with inversion at the pyramidal bridgehead atoms, C_1 and C_7. The transition state overlap integral $S_{1,7}$ is probably greater than 0.124, as our calculation used the ground state separation of atoms C_1 and C_7. The large overlap (S = 0.124) of the C_1 and C_7 π orbitals is attributable to the proximity of the bridgehead atoms; the corresponding transannular overlap in an ester of the cycloheptatriene, thujic acid,[11] is $S_{1,6}$ = 0.072 and the 1,3-overlap in *trans*-1,3-butadiene[11] is $S_{1,3}$ = 0.034. The mode of bromination of **1b** and of some other 1,4-dienes[1] is thus controlled by a significant olefinic homoconjugation;[12] the 1,5-bromination of these 1,4-dienes is reminiscent of the 1,4-bromination of the 1,3-diene cyclopentadiene.[13]

The ultraviolet spectra of **1a** and **1b** also demonstrate the overlap between the bridgehead π orbitals. Oxepin oxides **1a,b** display λ_{max} (EtOH) at 231[14] and 232 nm, respectively. The higher homologue of **1a**, containing four bridging methylenes between C_1 and C_7[14] (see Scheme I), is less strained and shows only end absorbtion (EtOH). Similarly, 9-oxabicyclo[3.3.1]non-1-ene, which has only one bridgehead double bond, absorbs at 190 nm.[15]

Diene **1b** lacks free rotation about the C_5–C_6 (and C_2–C_3) single bond (the dihedral angle H_5–C_5–C_6–H_6 is fixed, see Scheme I and Table I). The small vinyl-allylic coupling (H_6/H_5 or H_2/H_3) in transoid[3] **1b** supports our earlier finding[1] that the parent molecule, *sym*-oxepin oxide,[16] displays an average or preferred conformation which is flatter than the fixed transoid geometry of **1a** and **1b**. Other selected proton–proton couplings and angles are given also in Table I.

Experimental Section

Melting points are uncorrected and were determined on a Mel-Temp apparatus using open capillaries. Infrared spectra were recorded on a Perkin-Elmer 567 grating infrared spectrophotometer, using KBr disk or $CDCl_3$ solution film on a NaCl plate. ^1H-NMR spectra were determined on a Hitachi Perkin-Elmer R-22 (90 MHz) and a Jeol FX-60 Q (60 MHz) spectrometer; ^{13}C NMR spectra were determined on a Jeol FX-60 Q spectrometer. UV spectra were determined on a Perkin-Elmer Coleman 124 spectrophotometer; exact masses were measured on a CEC 110B Mattauch-Herzog (Dupont Instruments) high-resolution mass spectrometer.

Preparation of Oxepin Oxide 1b. The synthesis of **1b** from *syn*-2-hydroxyindane 3a,7a-oxide[2] followed the sequence previously detailed[1,16,17] for other arene oxide to oxepin oxide conversions. Thus, deprotection of an adduct diepoxide[1,16,17] (0.590 g, 1.05 mmol) and nitrogen extrusion from the corresponding azo compound[1,16,17] yielded oxepin oxide **1b** as a white, crystalline solid (0.138 g, 73% based on adduct diepoxide) after sublimation (70 °C (0.2 mmHg)). Data for **1b:** mp 90–91 °C; IR (film) 1665 (br), 1398, 1353, 1106 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ (Me_4Si) 2.29 (d of d, J = 9.8 and 11.5 Hz, 2 H_{ax}), 2.82 (d of d, J = 5.5 and 11.5 Hz, 2 H_{eq}), 3.65 (t of t, J = 5.5 and 9.8 Hz, H_9), (AA′XX′, H_3 and H_5), 5.05 (AA′XX′, H_2 and H_6); ^{13}C NMR ($CDCl_3$) δ_c (Me_4Si) 37.08 (t, J = 130 Hz, C_8 and C_{10}), 54.22 (d, J = 177 Hz, C_3 and C_5), 56.56 (q, J = 139 Hz, Me), 81.30 (d, J = 144 Hz, C_9), 110.14 (d, J = 166 Hz, C_2 and C_6), 163.97 (s, C_1 and C_7); UV (MeCN) λ_{max} (shoulder) 232 nm (ϵ 6.1 × 10^2); (EtOH) λ_{max} (shoulder) 232 nm (ϵ 6.1 × 10^2); M$^+$ m/e 180.079 (calcd 180.079).

X-Ray Crystal Analysis of Oxepin Oxide 1b. The crystal structure of **1b** was concluded in a routine manner. Suitable crystals were grown from petroleum ether utilizing the slow evaporation technique. The crystals were surveyed and a 1-Å intensity data set (maximum sin θ/λ = 0.5) was obtained on a Syntex P$\bar{1}$ diffractometer using copper radiation (λ = 1.5418 Å) at room temperature. The crystal density was measured by the flotation technique in aqueous KI. Final unit cell dimensions were obtained using 15 high-angle reflections ($2\theta > 54°$). The diffractometer was equipped with a graphite incident beam monochromator mounted in the perpendicular mode. During data collection a θ–2θ scan technique was employed, the scan rate was 2°/min in 2θ, the scan range was 1.0° below $K\alpha_1$ and 1.0° above $K\alpha_2$, and the background was counted for half the scan time on each side of the peak. A single check reflection was monitored every 30 reflections and indicated no crystal damage since it was reproducible within counting statistics.

The diffractometer output was processed using subprograms of the CRYM crystallographic computer system.[18] The processing included corrections for background, Lorentz, and polarization effects. The polarization effect due to the graphite monochromator was included in these corrections.[19] No corrections were made for absorption. The data processing also included calculation of the F^2 value and its standard deviation for each reflection. The standard deviations were assigned on the basis of the equation

$$\sigma^2(I) = S + \alpha^2(B_1 + B_2) + (dS)^2$$

where S is the scan count, B_1 and B_2 are the background counts, d is an empirical constant equal to 0.02, and α is the scan time to total background time ratio. All intensities with values less than three times the standard deviation were set equal to zero with zero weight. The data set was placed on an approximately absolute scale by means of Wilson statistics. Crystal parameters are summarized in Table II.

Determination of Structure and Refinement. A trial structure was obtained by direct methods using the MULTAN program.[20] This trial structure refined routinely to an acceptable R index (see Table II). The final cycles of full-matrix least-squares refinement contained all atomic coordinates, anisotropic temperature factors, scale factor, and secondary extinction factor in one matrix. The hydrogen positions were located by difference Fourier techniques. The hydrogen positions were included in the final cycles of refinement, but their temperature factors were not refined. Final shifts for the non-hydrogen atoms were all zero; shifts for the hydrogen atoms were all less than 0.2 of the standard deviation. The quantity minimized by the least-squares procedure was $\Sigma\omega(F_o^2 - F_c^2)^2$, where $\omega = 1/\sigma^2(F_o^2)$. A final difference Fourier revealed no missing or misplaced electron density. Nonhydrogen atomic parameters, hydrogen coordinates, atomic distances, atomic angles, and torsion angles for the molecule appear in Tables III–VII.[21]

Table II

A. Crystal Parameters	
formula	$C_{10}H_{12}O_3$ (180.2)
crystal size, mm	0.1 × 0.2 × 0.2
cell dimensions	
a, Å	5.2026 (7)
b, Å	12.301 (2)
c, Å	14.609 (2)
B, deg	101.44 (1)
V, Å	916.4 (2)
space group	$P2_1/c$
molecules/unit cell	4
density obsd, g/cm^3	1.31
density calcd, g/cm^3	1.306
linear absorption coefficient (μ), cm^{-1}	8.0
B. Refinement Parameters	
no. of reflections	941
nonzero reflections	859
R index ($R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$)	0.043
weighted R ($R' = \omega(F_o^2 - F_c^2)^2/\Sigma\omega F_o^4$)	0.0096

Slater-AO Overlap Calculations for Oxepin Oxide 1b. The π orbital at C_n (n = 1, 2, 6, and 7) was assumed to be a pure p orbital[10] whose axis is perpendicular to the plane defined by the three atoms bound directly to C_n. Thus, the direction cosines for each axis were determined from an orthogonalized and normalized set of atomic coordinates. Each overlap was calculated by summing the σ and π overlap contributions, each in turn calculated according to Mulliken.[9] By this procedure, the total overlap between C_1 and C_7 is S_{17} = 0.094(σ overlap) + 0.030(π overlap) = 0.124, and the total overlap between C_1 and C_2 is $S_{1,2}$ = 0.001(σ overlap) + 0.276(π overlap) = 0.277.

Bromination of Oxepin Oxide 1b. To a CH_2Cl_2 solution (1.0 mL) of **1b** (0.058 g, 0.32 mmol) at −78 °C was added a 0.78 M CH_2Cl_2 solution of Br_2 (0.45 mL, 0.35 mmol) over a period of 15 min. The resulting mixture was warmed to ambient temperature, rotary evaporated, and filtered through a short column of activity III silica gel (1:1 Et_2O–petroleum ether as eluent). Evaporation of the filtrate provided the white, crystalline, dibromodiepoxide **2b** (0.078 g, 71%). Data for **2b:** mp 160–163 °C dec; IR (KBr) 2975, 2930, 1241, 1101, 1089 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ (Me_4Si) 1.97 (d of d, J = 7.2 and 15.1 Hz, 2 H), 2.52 (br d, J = 15.1 Hz, 2 H), 3.28 (s, 3 H), 3.57 (br s, 2 H), 3.89 (br t, J = 7.2 Hz, 1 H), 4.42 (br s, 2 H); M$^+$ m/e 340.921 (calcd for $C_{10}H_{12}{}^{79}Br^{81}BrO_3 + H^+$ 340.921).

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Supplementary Material Available: Tables III–VII; non-hydrogen parameters, hydrogen coordinates, atomic distances, atomic angles, and torsion angles (5 pages). Ordering information is given on any current masthead page.

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