Hydrolysis of a Bromolactonic Acid

Richard D. Adams,*[1a] Daniel F. Chodosh,[1a] Martin Saunders,*[1a] and R. B. Woodward[1b]

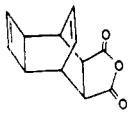
Departments of Chemistry, Yale University, New Haven, Connecticut 06520, and Harvard University, Cambridge, Massachusetts 02138

Received October 4, 1979

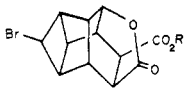
Hydrolysis of the bromolactonic acid formed from bromination of the maleic acid adduct of cyclooctatetraene is reported. Two products referred to as hydroxylactonic acid I and hydroxylactonic acid II have been isolated and characterized. Both products have the formula $C_{12}H_{12}O_5$ and each has been characterized by X-ray crystallographic methods. An X-ray crystallographic analysis of the bromolactonic acid has also been performed and is reported. Hydroxylactonic acid I is a homoallyl alcohol and hydroxylactonic acid II contains a cyclopropylcarbinyl alcohol. It is believed that both products are formed via an intermediate cyclobutyl cation. Both substances contain γ-lactone rings, even though the bromolactonic acid has a δ-lactone. It is suggested that release of strain in the bicyclooctane molecular framework accompanies rupture of the cyclobutyl ring in the bromolactonic acid and facilitates a γ- rather than a δ-lactone ring closure.

Introduction

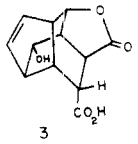
Maleic acid and its derivatives have long been known to form adducts with cyclooctatetraene. However, the molecular structure of these adducts has only recently been unambiguously established and shown to have the form **1**.[2] Because of the long period of uncertainty in the



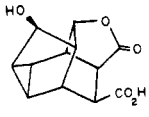
1



2



3



4

structure of the adducts, studies of their reactions with halogen have long been the source of confusion and controversy.[3] The problem now appears to have been resolved through the recent crystallographic analysis of the products from the bromination of the methyl ester of **1**.[12] Two products were observed. The major product (**2**, R = CH_3) has been formed through a bromine-induced diagonal coupling of the double bonds and the formation of a δ-lactone ring. The diagonal coupling produces an obvious strain on the bicyclooctane framework which may, in turn, be responsible for the δ-lactone ring closure.

Here we report our studies of the hydrolysis of the bromolactonic acid **2**, R = H. Both products and starting material have been characterized crystallographically and are described herein.

Results and Discussion

When treated with aqueous K_2CO_3 (reflux, 20 h), the bromolactonic acid lost bromine and yielded hydroxylactonic acid I, mp 223 °C, and hydroxylactonic acid II, mp 254–256 °C. Both compounds have the same empirical formula, $C_{12}H_{12}O_5$. Our X-ray crystallographic analyses of these products show that hydroxylactonic acid I has the structure **3** and hydroxylactonic acid II has the structure **4**.

Description of the Structures. Bromolactonic Acid. We have performed an X-ray crystallographic analysis of the bromolactonic acid and because of its direct relationship to the products have included a brief description of its molecular structure here. An ORTEP diagram[13] of the bromolactonic acid is shown in Figure 1 The molecule does not differ substantially from that of the methyl ester derivative **2**.[12] The important features are a carbon–carbon single bond, C(4)–C(5), which has been formed through a diagonal coupling of the double bonds in **1** and a δ-lactone ring, C(8)–C(9)–C(5)–C(12)–O(2)–C(10)–O(1), which has been formed by attack of a carboxylate group on C(12). An important consequence of the diagonal C–C coupling is the introduction of strain into the bicyclooctane framework, C(2)–C(3)–C(6)–C(7)–C(8)–C(9)–C(5)–C(12). This is readily seen by the twist of the two atom pair C(5)–C(12) with respect to the remaining six atoms in Figure 1. This twist may be responsible for the δ-lactone ring closure. The cyclobutane ring C(1)–C(2)–C(3)–C(4) is highly puckered with the dihedral angle of 42.5° being much larger than the value of 26 ± 3° generally found in simple substituted cyclobutanes.[14] It is probable that the trans ring fusion contributes significantly to this result.

Hydroxylactonic Acid I. An ORTEP drawing[13] of the molecular structure of hydroxylactonic acid I is shown in

(1) (a) Yale University; (b) Harvard University; deceased July 8, 1979.
(2) G. Filippini, G. Induni, and M. Simonetta, *Acta Crystallogr., Sect. B*, **29**, 2471 (1973).
(3) Much of the history dealing with electrophilic addition to cyclooctatetraene adducts of maleic acid derivatives is contained in the following papers.[4-12]
(4) W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Justus Liebigs Ann. Chem.*, **560**, 1 (1948).
(5) A. C. Cope, A. C. Haven, F. L. Ramp, and E. R. Trumbull, *J. Am. Chem. Soc.*, **74**, 4867 (1952).
(6) M. Auram, G. Matesscu, and C. D. Nenitzescu, *Justus Liebigs Ann. Chem.*, **636**, 174 (1960).
(7) R. C. Cookson, J. Hudec, and J. Marsden, *Chem. Ind.*, 21 (1961).
(8) M. Saunders, Ph.D. Thesis, Harvard University, 1956.
(9) T. Sasaki, K. Kanematsu, and A. Kondo, *J. Org. Chem.*, **39**, 2246 (1974).
(10) T. Sasaki, K. Kanematsu, and A. Kondo, *J. Org. Chem.*, **40**, 1642 (1975).
(11) T. Sasaki, K. Kanematsu, A. Kondo, and K. Okada, *J. Org. Chem.*, **41**, 2231 (1976).
(12) A. Kondo, T. Yamane, T. Ashida, T. Sasaki, and K. Kanematsu, *J. Org. Chem.*, **43**, 1180 (1978).
(13) C. K. Johnson, "ORTEP: A Fortran Thermal-Ellipsoid Plot Progam for Crystal Structure Illustrations", Oak Ridge National Laboratory, report no. ORNL-3794.
(14) F. A. Cotton and B. A. Frenz, *Tetrahedron*, **30**, 1587 (1974).

0022-3263/80/1945-2109$01.00/0

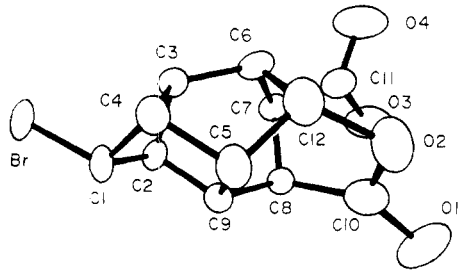


Figure 1. ORTEP diagram of the bromolactonic acid showing 50% probability ellipsoids.

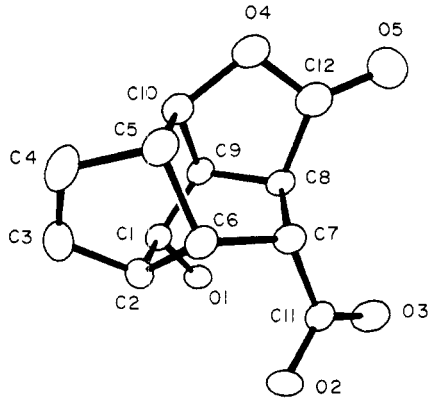


Figure 2. ORTEP diagram of hydroxylactonic acid I showing 50% probability ellipsoids.

Figure 2. The interesting features of this molecule are a double bond, C(3)-C(4) = 1.329 (3) Å, a γ-lactone ring, C(8)–C(9)–C(10)–O(4)–C(12)–O(5), and a hydroxyl group attached to C(1). Its formation from bromolactonic acid (Figure 1) can be envisaged as ionization of bromide forming a carbonium ion on C(1), elimination cleaving the bond between C(3) and C(4) and forming a double bond between C(4) and C(1), and quenching of the carbonium ion on C(3) by water. In the course of the reaction, the δ-lactone ring must have hydrolyzed, and a γ-lactone ring was formed with the other carboxyl group, O(4)–C(12)–O(5) (Figure 2). Finally, sometime in the course of the reaction, C(7) is epimerized. Figure 2 also shows that there is very little strain present in the bicyclooctane unit C(1)–C(2)–C(6)–C(7)–C(8)–C(9)–C(10)–C(5) of this molecule. In the crystal we found an intermolecular hydrogen bond between the carboxyl hydrogen atom and the hydroxyl oxygen, O(1)--H(12) = 1.65 Å, and a weaker hydrogen bond between one carboxyl oxygen atom and the hydroxyl hydrogen, O(3)--H(11) = 1.97 Å. The distances between the oxygen atoms involved in these hydrogen bonds are (O)1--O(2) = 2.689 (2) Å and O(1)--O(3) = 2.907 (2) Å, respectively.

Hydroxylactonic Acid II. An ORTEP drawing[13] of the molecular structure of hydroxylactonic acid II is shown in Figure 3. This molecule contains a cyclopropane ring, a γ-lactone ring, and a hydroxyl group bonded to C(1). This molecule can be formed from the bromolactonic acid (Figure 1) through loss of bromide, cleavage of the bond between C(3) and C(4), formation of a new bond between C(3) and C(1), and addition of a hydroxyl group to C(4). The γ-lactone ring is formed similarly to that in the hydroxylactonic I. Once again one can see that the bicyclooctane framework C(4)–C(5)–C(8)–C(9)–C(10)–C(3)–C(2)–C(7) contains no unusual distortion. In the crystal there are intermolecular hydrogen bonds between the carboxyl hydrogen atom the hydroxyl oxygen atoms, O(1)--H(12) = 1.83 Å, and the hydroxyl hydrogen and a carbonyl oxygen, O(2)--H(11) = 2.09 Å. The distances

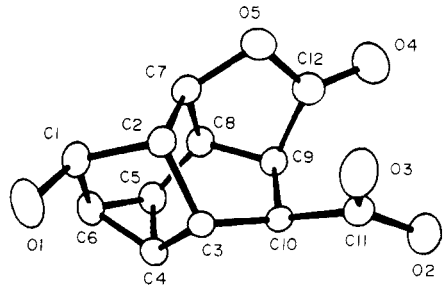


Figure 3. ORTEP diagram of hydroxylactonic acid II showing 50% probability ellipsoids.

between the oxygen atoms involved in these hydrogen bonds are O(1)--O(3) = 2.668 (1) Å and O(1)--O(2) = 2.792 (1) Å, respectively.

The hydrolysis products were obviously formed from the conversion of a cyclobutyl cation to homoallylic alcohol and cyclopropylcarbinyl alcohol groupings, respectively. Hydroxylactonic acid I has also undergone epimerization of a carboxyl group to give the trans stereochemistry which might be expected to be more stable. Interestingly, both compounds contain γ-lactone rings. It is reasonable to assume that under the basic reaction conditions the lactone ring in the bromolactonic acid is opened to yield a dicarboxylate. The Coulombic interaction of the two negative charges with the developing positive charge of the cyclobutyl cation should greatly stabilize the transition state. The rupture of the cyclobutane ring then relieves the distortion in the bicyclooctane framework and this, in turn, makes an *adjacent* γ-lactone ring closure rather than a *diagonal* δ-lactone ring closure preferable.

Experimental Section

^{13}C NMR spectra were recorded at the Southern New England High Field NMR Facility, operating at 67.88 MHz. The bromolactonic acid was prepared by an established procedure.[4] Its ^{13}C NMR spectrum showed resonances at (ppm vs. Me_4Si) 171.65, 170.41, 81.55, 47.19, 45.85, 40.91, 40.49, 38.62, 35.55, 29.86, 27.90 (missing resonance is probably Br-substituted carbon).

Preparation and Properties of Hydroxylactonic Acid I and Hydroxylactonic Acid II. The bromolactonic acid (11 g) was dissolved in a solution of 11 g of K_2CO_3 in 800 mL of water and refluxed for 20 h. The orange solution was acidified with HCl, refrigerated for 6 h, and filtered. The yellow filtrate was evaporated to dryness in vacuo and extracted with boiling chloroform several times. The chloroform extract yielded 0.24 g of hydroxylactonic acid I on recrystallization from EtOAc. The residue was extracted with boiling acetonitrile and yielded on recrystallization 1.3 g of hydroxylactonic acid II, mp 254–256 °C. Anal. Calcd for $C_{12}H_{12}O_5$: C, 61.01; H, 5.12. Found: C, 61.01; H, 5.14. ^{13}C NMR (ppm vs. Me_4Si) 175.18, 172.07, 77.33, 73.38, 38.05, 36.49, 31.02, 29.49, 19.09, 16.85, 6.91.

Diffraction Measurements. General Procedure. All measurements were made on an Enraf-Nonius CAD-4 circle automatic diffractometer with graphite monochromatized Mo K_α (0.71073 Å) radiation. Crystal surveys and unit-cell selections were made for each compound by using the search, centering, and automatic indexing routines of the CAD-4 system software and 25 randomly selected reflections. Final cell parameters were obtained by the centering and least-squares refinement of 25 high angle ($2\theta > 40°$) reflections. Crystal and intensity measurement data for the bromolactonic acid, hydroxylactonic acid I, and hydroxylactonic acid II are listed in Table I.

All structure-solving programs were from the Enraf-Nonius SDP progam library and all calculations were performed on a PDP 11/45 computer.

Bromolactonic Acid. A thick crystalline plate of dimensions 0.326 × 0.315 × 0.100 mm was cleaved from a larger plate and mounted in a thin-walled glass capillary. ω-Scan peak half-widths were generally 0.2° or less. A monoclinic unit cell was selected and the systematic absences $0k0$, $k = 2n + 1$, and $h0l$, $h + l =$

Table I. Experimental Data for X-ray Diffraction Measurements

	bromolactonic acid	hydroxylactonic acid I	hydroxylactonic acid II
	A. Crystal Parameters at 22 ± 2°		
space group	$P2_1/n$	$Pbca$	$P\bar{1}$
lattice constants	a = 8.131 (2) Å	a = 9.042 (2) Å	a = 6.529 (1), α = 83.30 (1) Å
	b = 11.922 (1) Å	b = 10.154 (2) Å	b = 7.331 (1), β = 86.61 (1) Å
	c = 11.685 (2) Å	c = 21.828 (3) Å	c = 10.745 (1), γ = 75.88 (1) Å
	β = 100.61 (2)°		
volume	1113.3 (7) Å^3	2004.0 (11) Å^3	499.9 (2) Å^3
mol wt	299.13	236.23	236.23
Z	4	8	2
ρ_{calcd} (g/cc)	1.785	1.566	1.569
	B. Measurement of Intensity Data		
reflections measured	$+h,+k,\pm l$	$+h,+k,\pm l$	$+h,+k,\pm l$
max 2θ	50°	50°	57°
scan type	couple θ(crystal) − 2θ(counter)	moving crystal-stationary counter	couple θ(crystal) - 2θ(counter)
scan speed, variable max	10.0°/min	10.0°/min	10.0°/min
min	1.25°/min	1.33°/min	1.25°/min
background	1/4 additional scan at each end of scan	1/4 additional scan at each end of scan	1/4 additional scan at each end of scan
crystal orientation	[010] 89.4° from φ axis	[010] 43° from φ axis	a* 77.1° from φ axis
std. reflections approximately every 100 data reflections	4% decrease	3% decrease	random fluctuation
total data collected	2175 including absences	2019 including absences	2543
data used	$F^2 > 3.0\sigma(F^2)$; 1366	$F^2 > 2.0\sigma(F^2)$; 1142	$F^2 > 3.0\sigma(F^2)$; 2147
	C. Treatment of Data		
absorption coeff, μ	39.15 cm^{-1}	1.326 cm^{-1}	1.329 cm^{-1}
grid	8 × 8 × 8		
transmission factors	max 0.673; min 0.091		
ignorance factor, p	0.03	0.03	0.03
decay correction	min 0.99; max 1.04	min 0.99; max 1.03	

$2n + 1$, allowed identification of the unique space group $P2_1/n$. Crystal faces were identified as (102), ($\bar{1}0\bar{2}$), (243), ($\bar{2}\bar{4}3$), (132), ($\bar{1}\bar{3}2$), (102), and (310), with the last being assigned to the cleavage face.

The structure was solved by a combination of Patterson and difference Fourier techniques. The position of the bromine atom was determined from a three-dimensional Patterson synthesis. Full-matrix least-squares refinement on this atom with an isotropic temperature factor produced the residuals

$$R = \frac{\sum||F_o| - |F_c||}{\sum|F_o|}$$

$$R_w = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2}\right]^{1/2}$$

of 0.437 and 0.549. The function minimized during refinement was $w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F_o)^2$. Neutral-atom scattering factors were calculated from the tables of Cromer and Waber.[15a] Anomalous dispersion corrections, f' and f'', were made for all nonhydrogen atoms.[15b] A difference Fourier synthesis revealed the positions of all remaining nonhydrogen atoms. An absorption correction was applied to the data at this time, using the Gaussian integration method and a grid of 8 × 8 × 8. Least-squares refinement with anisotropic temperature factors (β_{ij}'s) reduced the residuals to 0.075 and 0.095. Ten hydrogen-atom positions were calculated for the appropriate carbon atoms, assuming tetrahedral geometry and C-H distances of 0.95 Å. These hydrogen atoms were included in subsequent structure factor calculations (B = 5.0 Å^2), but their positions were not refined. Refinement converged after three additional least-squares cycles and produced the final residuals R = 0.042 and R_w = 0.056. A final difference Fourier synthesis was featureless. The largest peaks were 0.892, 0.842, and 0.579 e$^-$/Å^3 and were clustered about the bromine atom. The carboxyl hydrogen atom was not unambiguously located and no attempt to place it artificially was made. The value of the largest shift/error parameter on the final cycle of refinement was 0.01. The value of the standard deviation of an observation of unit weight was 2.765. The minimum transmission coefficient in the absorption correction occurred for the 406th reflection. The structure-factor calculation showed poor agreement for this and related $h0l$ reflections. These few reflections were, however, retained in the data set during the final refinements.

Hydroxylactonic Acid I. A crystal of approximate dimensions 0.35 × 0.30 × 0.10 mm was selected and mounted in a thin-walled glass capillary. ω-Scan peak half-widths were generally 0.3° or less. An orthorhombic unit cell was selected and the systematic absences $0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; $hk0$, $h = 2n + 1$ were identified the unique space group $Pbca$. The structure was solved by direct methods using the program MULTAN. An E-map based on the phases of 165 strong reflections (E_{min} = 1.65) revealed the positions of all nonhydrogen atoms. Least-squares refinement with anisotropic temperature factors (β_{ij}'s) yielded residuals R = 0.081 and R_w = 0.095. Hydrogen atoms on the oxygen atoms were next located in a difference Fourier synthesis. The remaining hydrogen atom positions were calculated. Hydrogen atom contributions were included in subsequent structure-factor calculations (B = 5.0 Å^2), but they were not refined. Refinement converged after three additional least-squares cycles and produced the final residuals R = 0.047 and R_w = 0.047. The largest shift/error value on the final cycle was 0.07. The error in an observation of unit weight was 1.847. A final difference Fourier synthesis showed no significant features. The largest peaks were approximately 0.3 e$^-$/Å^3.

Hydroxylactonic Acid II. A crystal of approximate dimensions 0.6 × 0.5 × 0.4 mm was mounted in a thin-walled glass capillary. ω-Scan peak half-widths were generally 0.15° or less. A triclinic unit cell was selected. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. The structure was solved by direct methods using the program MULTAN.[16] An E-map based on the phases of 232 strong reflections (E_{min} = 1.60) provided the coordinates of all nonhydrogen atoms. Hydrogen atom positions for the carbon atoms

(15) "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1975; (a) Table 2.2B, pp 99–101; (b) Table 2.3.1, pp 149–50.

(16) C. Germain, P. Main, and M. Woolfson, *Acta Crystallogr., Sect. A*, 27, 368 (1971).

Table II. Intramolecular Bonding Distance

atoms	distance, Å	atoms	distance, Å
	A. Bromolactonic Acid		
Br-C1	1.964 (3)	C6-C12	1.559 (4)
C1-C2	1.540 (4)	C7-C8	1.554 (4)
C1-C4	1.526 (4)	C7-C11	1.513 (4)
C2-C3	1.570 (4)	C8-C9	1.565 (4)
C2-C9	1.535 (4)	C8-C10	1.497 (4)
C3-C4	1.566 (4)	C10-O1	1.207 (4)
C3-C6	1.552 (4)	C10-O2	1.366 (4)
C4-C5	1.548 (4)	C11-O3	1.264 (4)
C5-C12	1.519 (4)	C11-O4	1.264 (4)
C5-C9	1.571 (4)	C12-O2	1.461 (4)
C6-C7	1.531 (4)		
	B. Hydroxylactonic Acid I		
O1-C1	1.456 (2)	C3-C4	1.329 (3)
O2-C11	1.322 (2)	C4-C5	1.504 (3)
O3-C11	1.220 (2)	C5-C6	1.561 (3)
O4-C10	1.474 (3)	C5-C10	1.543 (3)
O4-C12	1.354 (3)	C6-C7	1.548 (3)
O5-C12	1.205 (2)	C7-C8	1.556 (3)
C1-C2	1.549 (3)	C7-C11	1.521 (3)
C1-C9	1.543 (3)	C8-C9	1.537 (3)
C2-C3	1.516 (3)	C8-C12	1.509 (3)
C2-C6	1.547 (3)	C9-C10	1.545 (3)
		O1-H11[a]	0.95
		O2-H12[a]	1.05
	C. Hydroxylactonic Acid II		
O1-C1	1.451 (1)	C3-C10	1.549 (1)
O2-C11	1.239 (1)	C4-C5	1.511 (1)
O3-C11	1.301 (1)	C4-C6	1.503 (1)
O4-C12	1.206 (1)	C5-C6	1.534 (1)
O5-C7	1.468 (1)	C5-C8	1.525 (1)
O5-C12	1.359 (1)	C7-C8	1.525 (1)
C1-C2	1.536 (1)	C8-C9	1.553 (1)
C1-C6	1.509 (1)	C9-C10	1.575 (1)
C2-C3	1.566 (1)	C9-C12	1.517 (1)
C2-C7	1.537 (1)	C10-C11	1.517 (1)
C3-C4	1.528 (1)	O1-H11[a]	0.72
		O3-H12[a]	0.87

[a] Hydrogen atom positions were not refined.

Table III. Intramolecular Bond Angles for Bromolactonic Acid

atoms	angle, deg	atoms	angle, deg
Br-C(1)-C(2)	113.3 (2)	C(6)-C(7)-C(8)	104.0 (2)
C(2)-C(1)-C(4)	84.7 (2)	C(6)-C(7)-C(11)	115.0 (2)
Br-C(1)-C(4)	113.4 (2)	C(8)-C(7)-C(11)	112.6 (2)
C(1)-C(2)-C(3)	87.8 (2)	C(7)-C(8)-C(9)	107.7 (2)
C(1)-C(2)-C(9)	100.3 (2)	C(7)-C(8)-C(10)	106.1 (2)
C(3)-C(2)-C(9)	99.0 (2)	C(9)-C(8)-C(10)	107.8 (2)
C(2)-C(3)-C(4)	82.4 (2)	C(2)-C(9)-C(8)	111.0 (2)
C(2)-C(3)-C(6)	112.4 (2)	C(2)-C(9)-C(5)	98.2 (2)
C(4)-C(3)-C(6)	109.6 (2)	C(5)-C(9)-C(8)	110.5 (2)
C(1)-C(4)-C(3)	88.4 (2)	C(8)-C(10)-O(1)	128.6 (3)
C(1)-C(4)-C(5)	103.4 (3)	C(8)-C(10)-O(2)	111.9 (3)
C(3)-C(4)-C(5)	93.0 (2)	O(1)-C(10)-O(2)	119.5 (3)
C(4)-C(5)-C(9)	99.8 (2)	C(7)-C(11)-O(3)	118.2 (3)
C(4)-C(5)-C(12)	103.8 (2)	C(7)-C(11)-O(4)	119.3 (3)
C(9)-C(5)-C(12)	103.9 (2)	O(3)-C(11)-O(4)	122.4 (3)
C(3)-C(6)-C(7)	107.9 (2)	C(5)-C(12)-C(6)	101.2 (2)
C(3)-C(6)-C(12)	101.9 (2)	C(5)-C(12)-O(2)	110.4 (3)
C(7)-C(6)-C(12)	107.4 (2)	C(6)-C(12)-O(2)	114.3 (2)
		C(10)-O(2)-C(12)	112.8 (2)

were calculated on the basis of idealized geometry while hydrogen atoms on the appropriate oxygen atoms were obtained from a difference Fourier synthesis. Hydrogen atom contributions were included in subsequent structure-factor calculations (B = 5.0 Å^2), but they were not refined. Final least-squares refinement produced the residuals R = 0.046 and R_w = 0.074. The largest shift/error value on the final cycle was 0.03. The error in an observation of unit weight was 4.146. A final difference Fourier synthesis showed no significant features. The largest peaks were approximately 0.4 e$^-$/Å^3.

Table IV. Intramolecular Bond Angles for Hydroxylactonic Acid I

atoms	angle, deg	atoms	angle, deg
C10-O4-C12	108.4 (2)	C8-C7-C11	111.0 (2)
O1-C1-C2	111.4 (2)	C7-C8-C9	108.3 (2)
O1-C1-C9	105.5 (2)	C7-C8-C12	108.3 (2)
C2-C1-C9	109.9 (2)	C9-C8-C12	102.4 (2)
C1-C2-C3	108.7 (2)	C1-C9-C8	112.4 (2)
C1-C2-C6	107.7 (2)	C1-C9-C10	115.5 (2)
C3-C2-C6	101.6 (2)	C8-C9-C10	97.7 (2)
C2-C3-C4	110.3 (2)	O4-C10-C5	110.5 (2)
C3-C4-C5	110.0 (2)	O4-C10-C9	102.6 (2)
C4-C5-C6	101.6 (2)	C5-C10-C9	109.7 (2)
C4-C5-C10	106.7 (2)	O2-C11-O3	122.7 (2)
C6-C5-C10	108.8 (2)	O2-C11-C7	114.2 (2)
C2-C6-C5	99.3 (2)	O3-C11-C7	123.0 (2)
C2-C6-C7	113.6 (2)	O4-C12-O5	121.3 (2)
C5-C6-C7	112.8 (2)	O4-C12-C8	109.2 (2)
C6-C7-C8	109.6 (2)	O5-C12-C8	129.5 (2)
C6-C7-C11	116.5 (2)		

Table V. Intramolecular Bond Angles for Hydroxylactonic Acid II

atoms	angle, deg	atoms	angle, deg
O1-C1-C2	109.38 (6)	O5-C7-C2	113.21 (6)
O1-C1-C6	110.34 (7)	O5-C7-C8	105.35 (6)
C2-C1-C6	102.59 (6)	C2-C7-C8	106.69 (6)
C1-C2-C3	103.14 (6)	C5-C8-C7	110.77 (6)
C1-C2-C7	104.68 (5)	C5-C8-C9	114.85 (7)
C3-C2-C7	109.98 (6)	C7-C8-C9	97.77 (6)
C2-C3-C4	102.96 (5)	C8-C9-C10	108.94 (6)
C2-C3-C10	115.16 (5)	C8-C9-C12	100.53 (6)
C4-C3-C10	105.53 (6)	C10-C9-C12	108.77 (6)
C3-C4-C5	107.66 (6)	C3-C10-C9	109.36 (6)
C3-C4-C6	108.38 (6)	C3-C10-C11	115.27 (6)
C5-C4-C6	61.21 (5)	C9-C10-C11	112.18 (6)
C4-C5-C6	59.15 (5)	O2-C11-O3	123.85 (7)
C4-C5-C8	113.90 (6)	O2-C11-C10	120.69 (7)
C6-C5-C8	121.60 (7)	O3-C11-C10	115.46 (6)
C1-C6-C4	106.27 (6)	O4-C12-O5	122.06 (8)
C1-C6-C5	118.35 (7)	O4-C12-C9	129.31 (8)
C4-C6-C5	59.64 (5)	O5-C12-C9	108.63 (6)
		C7-O5-C12	108.53 (6)

Bond distances for all three structures with errors calculated from the inverse matrix obtained from the final cycle of refinement are listed in Table II. Bond angles (errors from inverse matrix) for the three structures are listed in Tables III–V. Final values of atomic fractional coordinates, thermal parameters, intermolecular contacts, and unit-weighted least-squares planes are available.[17]

Acknowledgment. We thank the National Science Foundation for partial support in the purchase of the diffractometer. Support of the Southern New England High Field NMR Facility through a grant from the Biotechnical Resources Progam of the National Institutes of Health is gratefully acknowledged. M.S. thanks the National Science Foundation for financial support.

Registry No. 2 (R = H), 67655-52-1; **3**, 73323-98-5; **4**, 73323-99-6.

Supplementary Material Available: Fractional coordinates, thermal parameters, intermolecular contacts, least-squares planes, and structure factor amplitudes for all three structures (50 pages). Ordering information is given on any current masthead page.

(17) See Supplementary Material.