Tableau 3. *Angles des liaisons intramoléculaires* (°)

C(2)—C(1)—C(10)	124,76	C(12)-C(11)-O(11)	112,54
C(1)—C(2)—C(3)	120,44	C(11)-C(12)-C(13)	112,86
C(2)—C(3)—C(4)	117,91	C(12)-C(13)-C(14)	108,51
C(2)—C(3)—O(3)	120,39	C(12)-C(13)-C(17)	115,37
O(3)—C(3)—C(4)	121,70	C(12)-C(13)-C(18)	115,15
C(3)—C(4)—C(5)	122,34	C(14)-C(13)-C(17)	98,45
C(4)—C(5)—C(6)	122,02	C(14)-C(13)-C(18)	113,23
C(4)—C(5)—C(10)	122,33	C(17)-C(13)-C(18)	109,63
C(6)—C(5)—C(10)	115,56	C(13)-C(14)-C(8)	114,67
C(5)—C(6)—C(7)	109,63	C(8)-C(14)-C(15)	119,31
C(6)—C(7)—C(8)	112,93	C(13)-C(14)-C(15)	103,04
C(7)—C(8)—C(9)	110,12	C(14)-C(15)-C(16)	104,93
C(7)—C(8)—C(14)	108,82	C(15)-C(16)-C(17)	105,15
C(9)—C(8)—C(14)	107,60	C(15)-C(16)-O(16)	110,76
C(8)—C(9)—C(10)	112,71	C(17)-C(16)-O(16)	110,83
C(8)—C(9)—C(11)	114,35	C(16)-C(17)-C(13)	101,91
C(10)-C(9)—C(11)	114,81	C(13)-C(17)-C(20)	113,20
C(1)—C(10)-C(5)	112,06	C(13)-C(17)-O(17)	109,28
C(1)—C(10)-C(9)	108,99	C(16)-C(17)-C(20)	114,55
C(1)—C(10)-C(19)	107,71	C(16)-C(17)-O(17)	110,35
C(9)—C(10)-C(5)	104,12	C(20)-C(17)-O(17)	107,45
C(5)—C(10)-C(19)	109,83	C(17)-C(20)-C(21)	116,44
C(9)—C(10)-C(19)	114,19	C(17)-C(20)-O(20)	123,50
C(9)—C(11)-C(12)	112,67	C(21)-C(20)-O(20)	120,05
C(9)—C(11)-O(11)	108,37	C(20)-C(21)-O(21)	113,24

Tableau 4. *Angles de torsion*

Cycle *A*

C(1)—C(2)	0,39
C(2)—C(3)	3,03
C(3)—C(4)	−3,55
C(4)—C(5)	0,62
C(5)—C(10)	2,56
C(10)-C(1)	−3,10

Cycle *B*

C(5)—C(6)	−59,55
C(6)—C(7)	51,49
C(7)—C(8)	−51,02
C(8)—C(9)	55,98
C(9)—C(10)	−58,54
C(10)-C(5)	61,41

Cycle *C*

C(8)—C(9)	−52,02
C(9)—C(11)	49,73
C(11)-C(12)	−49,94
C(12)-C(13)	53,03
C(13)-C(14)	−59,41
C(14)-C(8)	57,97

Tableau 4 (*suite.*)

Cycle *D*

C(13)-C(14)	48,91
C(14)-C(15)	−31,21
C(15)-C(16)	0,58
C(16)-C(17)	29,60
C(17)-C(13)	−47,97

Tableau 5. *Distances intermoléculaires inférieures à* 3,5Å

Notations: Dupont, Dideberg & Campsteyn (1972).

C(2)—O(21)	4/101	3,484 (4) Å
C(11)-O(16)	1/001	3,431
C(15)-C(18)	2/01ī	3,481
C(15)-O(11)	1/00ī	3,449
C(21)-O(16)	2/110	3,348
C(21)-O(17)	2/110	3,491
O(3)—O(16)	4/100	2,690
O(11)-O(16)	1/001	2,819
O(16)-O(21)	2/11ī	3,320
O(17)-O(21)	2/11ī	3,088

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4-Bromo-2,3-dicarbomethoxy-2-cyclohepten-1-one

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Abstract. $C_{11}H_{13}O_5Br$, monoclinic, $P2_1/c$, $a=8\cdot177$ (2), $b=13\cdot674$ (3), $c=11\cdot265$ (3) Å, $\beta=91\cdot48$ (2)°, $Z=4$, $D_m=1\cdot61$, $D_c=1\cdot61$ g cm^{-3}. Full-matrix least-squares refinement gave a final $R_1=0\cdot036$ for 2028 independent

observed diffractometer reflections. The ketonic configuration with bromination at the C4 position of the strained seven-membered ring system is established.

Introduction. Crystals of the title compound, recrystallized from $CHCl_3$, yielded the crystallographic data given above. The lattice parameters were determined from a least-squares refinement of the angular settings of 12 accurately centered reflections $(2\theta > 80°)$. Data were collected on a CAD-4 diffractometer with graphite-monochromated copper radiation $(\lambda = 1·5418$ Å). The crystal used for data collection was ground into a sphere 0·45 mm in diameter.

The diffracted intensities were collected by the $\omega-2\theta$ scan technique with a takeoff angle of 3·5°. The scan rate was variable and was determined by a fast (20° $\text{min}^{-1})$ pre-scan. If 30 or more net counts were obtained, a slow scan was set to collect approximately 4000 net counts (subject to the constraint that the slow scan take no longer than 300 s). Background counts were collected for 25% of the total scan time at each end of the scan range. For each intensity the scan width was determined by the equation

$$\text{scan range} = A + B \tan \theta$$

where $A = 0·9°$ and $B = 0·4°$. Aperture settings were determined in a like manner with $A = 4$ mm and $B = 4$ mm. As a check on the stability of the diffractometer and the crystal, two reflections, 120 and 10,0,2 were measured at 30 min intervals during data collection. No significant variation in the reference intensities was noticed.

All reflections in the $hkl-hk\bar{l}$ and $h\bar{k}l-h\bar{k}\bar{l}$ quadrants with 2θ less than 140° were measured. After averaging, 2028 unique reflections with intensities greater than background were obtained. The intensities were then corrected for Lorentz, polarization, and absorption effects $(\mu = 50·1$ $\text{cm}^{-1})$.

The function $w(|F_o| - |F_c|)^2$ was minimized (Busing, Martin & Levy, 1962). No corrections were made for extinction. Neutral atom scattering factors for Br, O

and C were taken from the compilations of Cromer & Waber (1965); those for H were from *International Tables for X-ray Crystallography* (1962). The scattering by Br was corrected for the real and imaginary components of anomalous dispersion using Cromer's (1965) table.

The structure was solved by standard heavy-atom techniques, and refined by the least-squares method with isotropic temperature factors to $R_1 = \sum|F_o| - |F_c|/ \sum|F_o| = 0·16$. Refinement with anisotropic thermal parameters and the application of a weighting scheme $(w = 1/\sigma^2)$ gave $R_1 = 0·062$. The hydrogen atoms were found on a difference Fourier map, and further refinement (including the positional parameters of the hydrogen atoms) led to the final agreement indices $R_1 = 0·036$, $R_2 = \{\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2\}^{1/2} = 0·035$, and erf $= \{\sum w(|F_o| - |F_c|)^2/(m-s)\}^{1/2} = 1·60$ for $m = 2028$ observations and $s = 193$ parameters. The largest parameter shifts in the last cycle of refinement were less than 0·05 of their estimated standard deviations. A final difference Fourier synthesis indicated no unaccounted electron density. The final parameters are listed in Tables 1 and 2; the table of $|F_o|$ and $|F_c|$ is available on request.*

Discussion. Mild hydrolysis of the ring expansion product of the reaction of 1-morpholino- or 1-pyrrolidinocyclopentene with dimethyl acetylenedicarboxylate yields 1-hydroxy-2,3-dicarbomethoxy-1,3-cycloheptadiene (I) (Huebner, Dorfman, Robinson, Donoghue, Pierson & Strachan, 1963). It has been shown that this enolic structure (I) is favored at equilibrium over the tautomeric keto structure (II) (Hirsch & Cross, 1971). Electrophilic bromination of (I) yields a product, m.p. 73–74°, with an elemental analysis consistent with the formula $C_{11}H_{13}O_5Br$. Of the several reasonable struc-

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* This table has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30460 (35pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Final fractional coordinates and thermal parameters* $\times 10^4$

$$B = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)].$$

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	0·65978 (5)	0·87259 (4)	0·0787 (4)	220	103	90	−79	3	5
O(1)	0·3513 (3)	0·5233 (2)	0·1451 (2)	236	50	147	−10	−40	24
O(2)	0·0276 (2)	0·6741 (2)	0·0704 (2)	102	101	107	−11	16	−11
O(3)	0·1757 (2)	0·6153 (2)	−0·0772 (2)	129	62	85	−3	−22	−18
O(4)	0·2118 (3)	0·9333 (2)	0·1004 (2)	251	53	94	41	−21	−15
O(5)	0·1991 (2)	0·8357 (1)	−0·0597 (2)	137	54	64	18	−23	−1
C(1)	0·4892 (4)	0·8201 (2)	0·1825 (3)	125	59	63	−13	−3	−6
C(2)	0·5615 (4)	0·7520 (3)	0·2764 (3)	129	85	60	−2	−17	−3
C(3)	0·6665 (4)	0·6674 (3)	0·2357 (3)	132	92	89	14	−26	4
C(4)	0·6005 (4)	0·6120 (3)	0·1265 (3)	146	71	99	34	−11	−1
C(5)	0·4193 (4)	0·5997 (2)	0·1240 (3)	154	51	78	6	−25	−1
C(6)	0·3173 (3)	0·6866 (2)	0·0848 (2)	102	48	64	2	−5	−3
C(7)	0·3546 (3)	0·7808 (2)	0·1032 (2)	103	49	57	3	−2	−1
C(8)	0·1559 (3)	0·6592 (2)	0·0268 (3)	111	47	79	−4	−8	5
C(9)	0·2467 (3)	0·8594 (2)	0·0499 (3)	119	51	70	5	−0	1
C(10)	0·0782 (4)	0·8996 (3)	−0·1164 (4)	155	67	110	16	−46	12
C(11)	0·0262 (5)	0·5886 (4)	−0·1421 (4)	173	105	116	−27	−42	−24

A C 30B – 12*

Table 2. *Hydrogen atom positions (an isotropic* $B=$
5·0 Å^2 *assumed)*

	x/a	y/b	z/c
H(1C1)	0·447 (5)	0·879 (3)	0·216 (4)
H(2C2)	0·463 (5)	0·729 (3)	0·319 (4)
H(3C2)	0·631 (5)	0·794 (3)	0·339 (4)
H(4C3)	0·678 (5)	0·615 (3)	0·299 (4)
H(5C3)	0·778 (5)	0·689 (3)	0·221 (4)
H(6C4)	0·630 (4)	0·655 (3)	0·050 (3)
H(7C4)	0·645 (5)	0·544 (3)	0·136 (4)
H(8C10)	−0·027 (5)	0·878 (3)	−0·069 (4)
H(9C10)	0·136 (5)	0·962 (3)	−0·132 (4)
H(10C10)	0·039 (5)	0·868 (3)	−0·185 (4)
H(11C11)	−0·029 (5)	0·648 (3)	−0·163 (4)
H(12C11)	−0·058 (5)	0·573 (3)	−0·097 (4)
H(13C11)	0·061 (5)	0·542 (3)	−0·210 (4)

tures for the product, the absence of proton-magnetic-resonance signals for enolic or vinyl protons and the presence of an infrared absorption at 1680 cm^{-1} (conjugated C=O) indicated (III) or (IV) to be most likely. We now report X-ray crystallographic data verifying structure (III) as theproduct of the electrophilic bromination of (I).

(I)
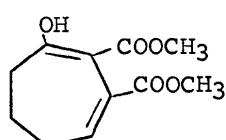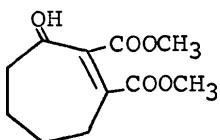
(II)
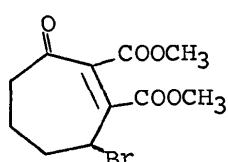
(III)
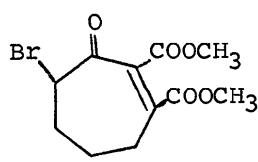
(IV)

The most striking feature of the structure is the prevalence of large angles within the cycloheptenone ring. Of the seven interior angles only the one at C(5) is smaller than one would predict on the basis of classical hybridization arguments. Since the intra-ring bond angles could only be reduced by steric repulsions among the substituent groups, one must assume that the angles are indicative of a highly strained system.

The Br–C(1) distance [1·977 (3) Å] is rather longer than the normal bromine–carbon length. Those tabulated by Sutton (1965) average 1·94 Å, and Wetherington & Moncrief (1973) have found 1·957 Å in the well determined structure of *anti*-α-bromoacetophenone oxime. The C–H bond lengths range from 0·89 to 1·07 Å with a σ of 0·05 Å.
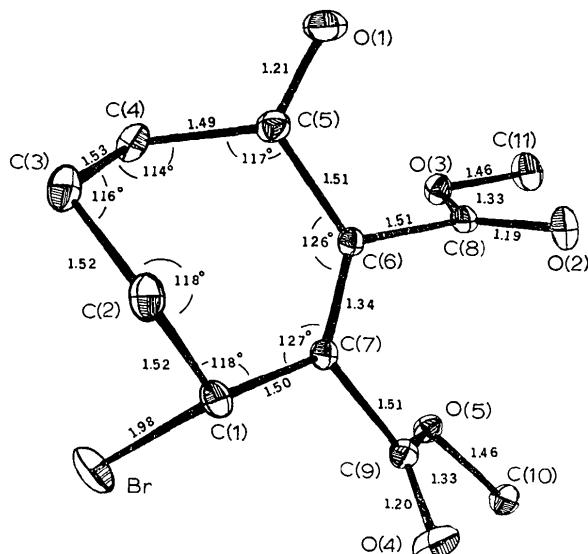

Fig. 1. 4-Bromo-2,3-dicarbomethoxy-2-cyclohepten-1-one with the atoms displayed as their 50 % probability ellipsoids for thermal motion. The estimated standard deviations in bond length are less than 0·004 Å. Bond angles not shown include:

Br—C(1)–C(2)	111·5 (2)°	Br—C(1)–C(7)	107·3 (2)°
O(1)–C(5)–C(6)	118·9 (3)	C(4)–C(5)–O(1)	123·7 (3)
C(5)–C(6)–C(8)	113·8 (3)	C(8)–C(6)–C(7)	120·0 (3)
C(9)–C(7)–C(1)	113·3 (3)	C(6)–C(7)–C(9)	119·8 (3)
C(6)–C(8)–O(2)	123·6 (3)	C(7)–C(9)–O(4)	123·9 (3)
C(6)–C(8)–O(3)	111·7 (3)	C(7)–C(9)–O(5)	110·6 (3)
O(2)–C(8)–O(3)	124·8 (3)	O(4)–C(9)–O(5)	125·5 (3)
C(8)–O(3)–C(11)	115·9 (3)	C(9)–O(5)–C(10)	116·2 (3)

The only non-bonding distances of note are the intermolecular distances less than 4·0 Å to the bromine atom; these are Br–O(1)=3·74, Br–C(4)=3·88, and Br–C(5)=3·91 Å.

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