Nuclear Magnetic Resonance Studies on the Monochloroketen–Cyclopentadiene Adduct, 7-*endo*-Chlorobicyclo[3,2,0]hept-2-en-6-one, and Crystal and Molecular Structure of the Derived 6-*endo*-Ol *p*-Bromobenzoate

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Summary The monochloroketen–cyclopentadiene adduct is 7-*endo*-chlorobicyclo[3,2,0]hept-2-en-6-one

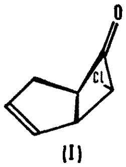
THE recent suggestion that the adduct 7-chlorobicyclo-[3,2,0]hept-2-en-6-one[1] has the chloro-group *endo* as in (I)[2] prompts us to report our *X*-ray and spectroscopic evidence leading to the same conclusion We required the relative configuration for a study of the ring-contraction of some 2-chlorocyclobutanols [3]

The 100 MHz n m r spectrum of the adduct[4] was complicated by long-range and virtual coupling, but the homogeneity (g l c) was confirmed by the single signal for 7-H Simultaneous irradiation of the olefinic and allylic methylene protons simplified the signals due to the remaining protons on the cyclobutanone ring to a deceptively simple[5] ABX pattern (respectively, 5-H, 1-H, and 7-H) with the following parameters

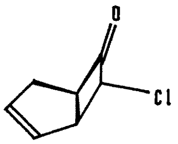
$$\delta_{1,5} = 3\ 9\,\text{Hz}, J_{1,5}|6\ 7|\text{Hz}, J_{1\ 7} \pm 9\ 4\,\text{Hz}, J_{5\ 7} \pm 1\ 6\text{Hz}$$

Significantly, the cross-ring (5,7) coupling has the same sign as the vicinal coupling (1,7), and the latter is assumed positive 5-H and 7-H must be *cis* for a positive cross-ring coupling constant,[6] and therefore the chloro-group must have the *endo*-configuration

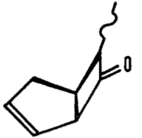
In order to confirm our assignment of configuration in the monochloroketen adduct (I) we prepared a suitable derivative for *X*-ray analysis Reduction of the keto-group by $NaBH_4$ gave a single alcohol† (later shown to be *endo*) Crystals of the *p*-bromobenzoate, m p 79—80°, grown from methylene chloride–methylcyclohexane solution, are monoclinic needles having space group $P2_1/c$, with lattice parameters $a = 18\ 488 \pm 0\ 009$, $b = 5\ 483 \pm 0\ 005$, $c = 13\ 393 \pm 0\ 007$ Å, $\beta = 94\ 00 \pm 0\ 06°$, D_m 1 606, D_c 1 607 g/cm^3 *X*-Ray intensity measurements were made using a Hilger and Watts four-circle *X*-ray diffractometer,



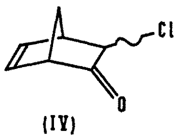
(I)



(II)



(III)



(IV)

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† As the alcohol could be oxidised back to (I) with chromic acid, no rearrangement was occurring at this step.

employing Mo radiation (Nb filter), with sin θ/λ (max) = 0 53, 1656 reflections were measured, 683 being below the threshold value

The structure was solved using Patterson and Fourier methods and the structure parameters were refined by full-matrix anisotropic least-squares procedures All hydrogen atoms were located on a Fourier difference-map and were included in the calculations with isotropic temperature factors The conventional *R* factor is at present 0 067 for the observed reflections E s d 's of atomic positions are 0 005—0 012 Å for carbon and oxygen atoms, e s d 's of bond lengths are 0 008—0 016 Å, and of bond angles are 0 6—1 0° (excluding hydrogen atoms) The results show that this derivative is 7-*endo*-chlorobicyclo-[3,2,0]hept-2-ene-6-*endo*-ol *p*-bromobenzoate

The chlorine and ester function oxygen atoms are attached to the cyclobutane ring in the *endo*-configuration (Figure) The cyclobutane ring is not planar, and may be regarded as folded along the line C-1–C-6, so that C-7, to which the chlorine atom is attached, is 0 283 Å out of the plane C-1, C-5, C-6 and is displaced away from the cyclopentene ring, the angle between the two planes through C-1, C-5, C-6 and C-1, C-7, C-6, respectively, is 15 3° The chlorine atom is 0 671 Å out of the plane C-1, C-5, C-6, and 1 314 A out of plane of C-1, C-6, C-7 The distances from O-1 to C-2, C-3, and C-4 are 3 306, 3·133, and 2 729 Å, respectively

The cyclopentene ring is in the envelope conformation, the distances of C-1, C-2, C-3, and C-4 from the least-squares plane through them are not greater than 0 007 Å, but C-5 is 0 196 Å above this plane, in the *endo*-conformation, the plane through C-1, C-4, C-5 is rotated through 12 6° out of the least-squares plane through C-1, C-2, C-3, and C-4 From the Table of torsion angles it can be seen that the folding of the cyclobutane ring along a diagonal, in conjunction with the envelope conformation of the cyclopentene ring, results in approximately equal degrees of torsion, about the bond C-5–C-1, between C-4 and C-6, and between C-2 and C-7.

Torsion angles

First atom	Second atom	Bond vector	Torsion angle (°)
C 4	C-6	C-5→ C-1	−118 6
4	7	,,	−129 4
4	2	,,	− 12 3
6	7	,,	− 10 8
2	7	,,	−117 1
2	5	C-3→ C-4	− 6 6
3	5	C-2→ C-1	+ 8 6
Cl	O-1	C-7→ C 6	− 21 9

From these results, the adduct formed between chloroketen and cyclopentadiene is (I), 7-*endo*-chlorobicyclo-[3,2,0]hept 2-en-6 one, and not (II), (III), or (IV).

The distances of the carbon atoms of the benzene ring from the least-squares plane through them are not greater than 0 004 Å With the exception of the two oxygen atoms, the rest of the *p*-bromobenzoate group and C-6 of the cyclobutane ring are within 0 046 Å of this plane, O-1 lies 0 066 Å above this plane and O-2 is 0 132 Å below it, corresponding to a small degree of twist about the bond C-8–C-9 The average benzene-ring C–C distance is 1 380 ± 0 019 Å, the spread in the individual observed values may be a consequence of the preponderance of bromine atoms in the immediate vicinity of the benzene ring carbon atoms, *e g* C-13 has five bromine neighbours at distances of less than 4 7 Å

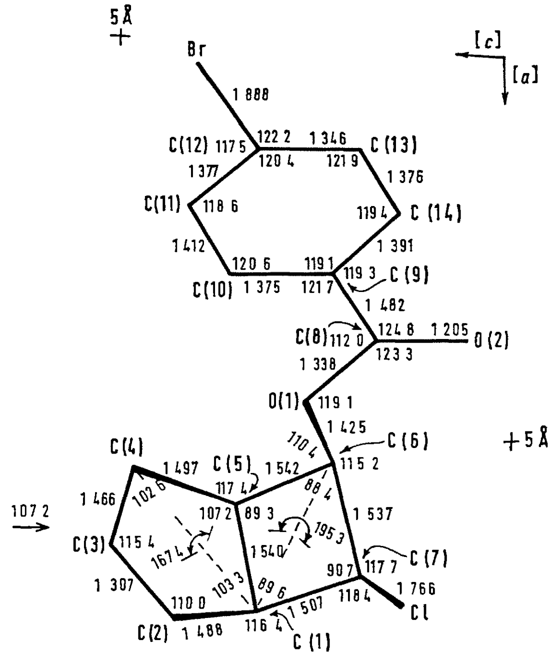

FIGURE *Projection of the molecule along the* b *axis, showing bond distances* (Å) *and angles* (*degrees*)

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[2] W T Brady E F Hoff, jun R Roe jun and F H Parry, jun , *J Amer Chem Soc* , 1969, **91**, 5679

[3] P R Brook *Chem Comm* 1968, 585

[4] We thank Dr J Feeney of Varian Associates for the 100 MHz spectra

[5] E D Becker, High Resolution N M R ," Academic Press New York, 1969 p 161

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