Structure and Chemistry of the Conformationally Rigid Dihalogenocyclobutane Unit of 6,7-Di-iodobicyclo[3.1.1]heptane; *X*-Ray Structure of 6,7-Di-iodobicyclo[3.1.1]heptane

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Summary The diaxial isomer (II) of 6,7-di-iodobicyclo-[3.1.1]heptane has been prepared by addition of iodine to tricyclo[4.1.0.0^{2,7}]heptane; the structure of (II), which does not undergo substitution by carbon nucleophiles, has been determined by single crystal *X*-ray diffraction.

Addition of I_2 to tricyclo[4.1.0.0^{2,7}]heptane (I) gives, in 55% isolated yield, a di-iodide whose structure we have established by single crystal *X*-ray diffraction to be the diaxial isomer (II) of 6,7-di-iodobicyclo[3.1.1]heptane. This product is consistent with the documented preference of bicyclobutanes for *cis* halogenation,[1] and with Masamune's tentative conclusion[2] of addition with inversion in the bromination of a similar compound.†

Crystal data: $C_7H_{10}I_2$, M 347·96, monoclinic, space group $P2_1/n$, a = 6·277(1), b = 15·459(3), c = 10·056(2) Å, β = 106·48(2)°, U = 935·74 Å^3, D_m = 2·44, D_c = 2·470 g cm^{-3},

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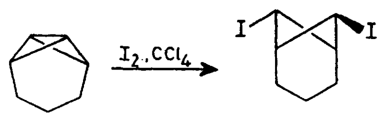
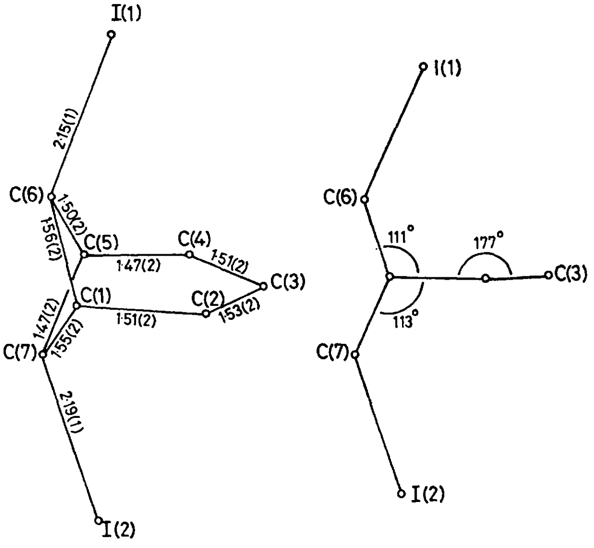
† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. The structure factor table may be obtained as a supplementary publication (No. 22073, 11 pp.) from the British Library. For details of obtaining this material, see Notice to Authors No. 7, Index Issues of *J.C.S. Perkin I* or *II*, 1976.



(I) (II)

Z = 4, Mo-K_α radiation (λ 0·71069 Å). Intensity data were collected on an automated diffractometer and corrected for Lorenz and polarization factors, and were rescaled to account for crystal decomposition (av. 35%) by monitoring three standards. The structure was solved by Patterson and Fourier techniques and refined by full-matrix least-squares analysis varying positional and anisotropic thermal parameters for nonhydrogen atoms and including hydrogens in idealized geometries. At convergence, conventional and weighted R values were 0·066 and 0·088, respectively, for 1684 independent reflections with $|F_0| > 3\,\sigma\,(|F_0|)$. It was evident from visual inspection that the crystal was subliming anisotropically during data collection which made it impractical to apply an absorption correction. This is probably the largest source of error in the refinement since the linear absorption coefficient is 67·22 cm^{-1}; however the major structural conclusions remain valid.

The structure of the unsubstituted hydrocarbon, bicyclo[3.1.1]heptane, has been solved by electron diffraction[3] and can be compared with that of (II), illustrated in the Figure. Dihedral angles about the four-membered ring are nearly identical for the two molecules but the considerable steric requirements of the iodine atoms have consequences for the conformation of the three-carbon bridge. Thus, the atoms C(1), C(2), C(3), C(4), and C(5) of (II) lie nearly in a plane while the corresponding bridge of the hydrocarbon is puckered by 37°.



Figure

The most interesting feature of (II) is its complete resistance to substitution by carbon nucleophiles. Attempts to introduce carbon substituents at C(6) by a variety of methods are summarized in the Table. In all cases either (II) was recovered unchanged or was reconverted into (I). For the reaction involving NaCN in ethanol, formation of ethyl carbamate probably results from ethanolysis of intermediate cyanogen or cyanogen iodide and this requires that the formal role of CN^- is that of a reducing agent. The mechanism apparently involves nucleophilic attack on iodine by CN^- and loss of the remaining halogen as I^-. The alternative mechanism, simple electron transfer, is ruled out by the fact that the half-wave potential for reduction of (II) (*ca.* $-1 \cdot 0$ V *vs.* Ag–AgCl) is > 2 V negative from the oxidation potential of CN^-.

Table

Reagent	Reaction conditions	Product
$NaCH(CO_2CH_2Me)_2$	Me_2SO, 5 h[a]	c
$NaCH_2SOMe$	Me_2SO, 2 h[a]	c
1,3-Dithiacyclohexan-2-yl-lithium	THF, 48 h[a]	c
$LiCH_2SPh$	THF, 20 h[a]	(I)
NaCN	EtOH–H_2O, 4 h[b]	(I) + $EtOCONH_2$
NaCN	Me_2SO, 1 h[a]	(I) (100%)

[a] Reaction performed at 25 °C. [b] Reaction performed at 80 °C. [c] No reaction; unchanged (II) was recovered. THF = tetrahydrofuran.

Nucleophilic attack on suitably[3] activated halogens by organolithium reagents and certain enolates is known.[4] This is the first example, to our knowledge, involving CN^-. The behaviour of (II) may be governed by the fact that normal, back-side approach to the iodine-bearing carbon atoms is blocked by the opposing bridge and that the stereochemistry is ideal for concerted loss of both iodine atoms. Stereoelectronic interaction between the halogens also greatly facilitates cathodic reduction of (II) which occurs 1 V more readily than reduction of 2-iodopentane.

The stereochemistry of iodination of (I) remains to be explained. We are inclined to believe that the same steric effects which prevent nucleophilic attack on the *exo* side of the four-membered ring in (II) are also important in determining the direction of addition of iodine to (I).

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