Stereochemistry of Seven-membered-ring Compounds: *X*-Ray Analysis of Dextrorotatory 4-Bromo-6,10-dimethylbicyclo[5,3,0]decan-3-one

By T. SATO, H. MINATO, M. SHIRO, and H. KOYAMA

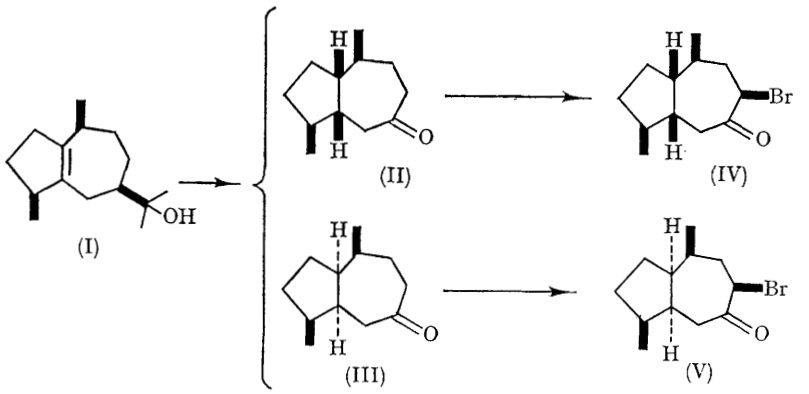
(*Shionogi Research Laboratory, Shionogi & Co., Ltd., Fukushima-ku, Osaka, Japan*)

THE conformations of seven-membered rings are of current interest (*e.g.*, Hendrickson[1,2]). Bromination of dextro- or laevo-rotatory 6,10-dimethylbicyclo[5,3,0]decan-3-one (II or III), prepared from guaiol (I) by Takeda and co-workers,[3] gave us the corresponding bromo-ketones (IV), m.p. 93—94°, or (V) (b.p. 84—85°/0·01mm.) respectively.

The conformational problem is complicated by the flexibility of seven-membered rings. Moreover, although the bromine atom of (IV) was expected on i.r., u.v., and o.r.d. evidence[4] to occupy an axial position, some uncertainty obtained. We have therefore carried out an *X*-ray crystal-structure analysis of the bromo-ketone (IV).

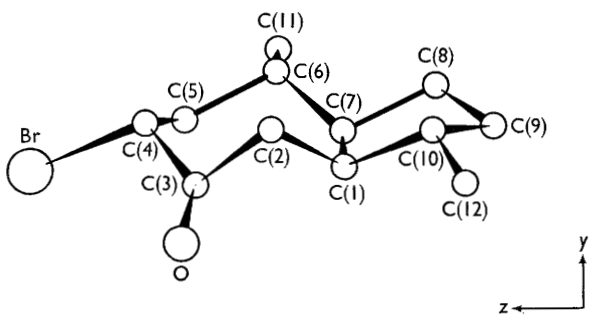
Dextrorotatory 4-bromo-6,10-dimethylbicyclo-[5,3,0]decan-3-one was crystallised from light petroleum at room temperature.

$C_{12}H_{19}OBr$, $M = 259{\cdot}2$, *Orthorhombic*, $a = 98{\cdot}73$, $b = 5{\cdot}09$, $c = 13{\cdot}27$ Å, $U = 1265$ Å^3, $D = 1{\cdot}363$, $z = 4$, $D_c = 1{\cdot}361$. *Space group* $P2_12_12_1$ (No. 19).



The three-dimensional intensity data were collected on a Hilger–Watts linear diffractometer, using Mo-K_α radiation with balanced filters. In the sets *h*0*l* to *h*4*l*, 743 independent reflexions had intensities in excess of their own standard deviation, and these were used, with Sim's weighting scheme, to solve the structure by the heavy-atom method. Refinement, which was by full-matrix least-squares analysis, was based on only 249 reflexions, and has been taken to an *R*-value of 10·0%. The other reflexions, whose intensities seemed liable to greater error, either because they were less than five times their standard deviation or because of possible extinction in the case of certain low-order reflexions, were excluded.

The structure of the molecule, as it exists in the crystal, is shown in the Figure. The bromine atom is equatorial. Molecular packing seems to be dominated by a close C=O · · · · C contact, with O · · · · C = 2·90 Å, across a two-fold screw axis.



FIGURE

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[1] J. B. Hendrickson, *J. Amer. Chem. Soc.*, 1961, **83**, 4537.
[2] J. B. Hendrickson, *Tetrahedron*, 1963, **19**, 1387.
[3] K. Takeda, H. Minato, T. Terasawa, and C. Yanailhara, *Chem. and Pharm. Bull.* (*Japan*), 1965, **13**, 942.
[4] K. Takeda, H. Minato, T. Terasawa, M. Ishikawa, and C. Yanaihara, *J. Chem. Soc.*, to be published.