CRYSTAL STRUCTURE AND FRAGMENTATION OF 15-EROMOLONGIBORNANE-8,9-DIONE. A STEREOSPECIFIC ROUTE TO <u>cis</u>-BICYCLO [5.4.6] UNDECAMES

Goverdhan Mehta* and Surinder K. Kapoor

Department of Chemistry,
Indian Institute of Technology, Kanpur-208016, India

T. N. Guru Row and K. Venkatesan*

Department of Organic Chemistry, Indian Institute of Science, Bangalore-560012, India (Received in UK 3 June 1974; accepted for publication 19 June 1974)

The diversity of carbocyclic structures encountered among the sesquiterpene group of natural products has been attributed to stereoelectronically controlled, C+- The type of in vivo cyclisation of farnesyl pyrophosphate (FPP) on the enzyme surface. A biogenetically interesting example is the cyclisation of bicyclic ion (I)² derived from FPP to the tricyclic sesquiterpenes of longifolene, longibornane and longipinane class. The important provise of this sterically controlled internal cyclisation is the cis-stereochemistry of the ring junction in the ion (I). In order to simulate the biogenetic type cyclisations of a species related to (I), a stereospecific creation of cis-bicyclo[5.4.0] undecane bearing requisite functionality and substitution pattern was contemplated. An efficient synthesis of cis-bicyclo[5.4.0] undecane derivative (III) via a novel Grob type fragmentation of 15-bromolongibornane-8,9-dione (IV) as well as the crystal structure of (IV) are reported here.

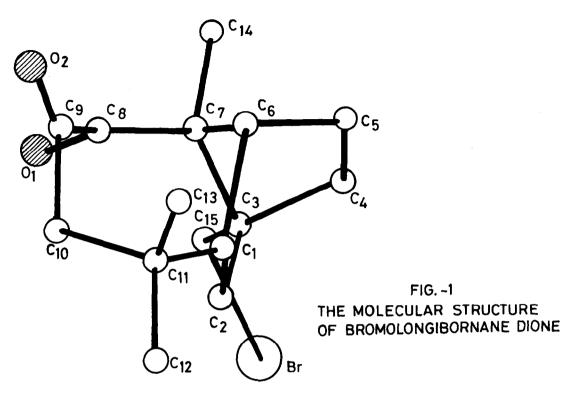
$$\begin{array}{c} H \\ \downarrow \\ H \end{array}$$

$$\begin{array}{c} CH_2-Br \end{array}$$

$$\begin{array}{c} (II)R=H \\ (IV)R=0 \end{array}$$

$$\begin{array}{c} H \\ \downarrow \\ H \end{array}$$

$$\begin{array}{c} (III) \\ (III) \end{array}$$



diffraction were orthorhombic and belonged to space group $P2_1^2_1^2_1$. The unit cell parameters are a=20.07(2), b=10.05(2), c=7.31(1) Å and calculated density indicated four molecules per unit cell. A three dimensional Patterson synthesis computed for the observed data (1038 reflections) using CuK_K radiation (1.5418Å) gave the position of the heavy atom and led to structure (IV, Fig. 1).

The reaction of (IV) with Zn dust in IMF (14 hr at 150°) led to the expected fragmentation reaction and resulted in the isolation (silica-gel) of <u>cis</u>-diketone (III) in 57% yield. The structure of this product is fully supported by its spectral parameters: $2^{C=0}$ 1715 cm⁻¹, $2^{C=CH_2}$ 885, 1645 and 3130 cm⁻¹, $3^{C=0}$ 0.98 (6H, s, <u>gem</u>-dimethyl), 1.02(3H, d, J=6 Hz, CH₃-C-H), 4.83(2H, broad, H_2 C=C-). The results of the Lewis acid catalysed cyclization of the enol acetate⁵ of (III) will be reported elsewhere.

REFERENCES

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- 4. There are several interesting and noteworthy features of this X-ray crystal study. They will be detailed elsewhere.
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