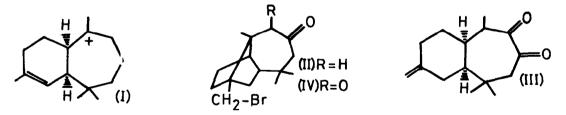
CRYSTAL STRUCTURE AND FRAGMENTATION OF 15-BROMOLONGIBORNANE-8,9-DIONE. A STEREOSPECIFIC ROUTE TO CIS-BICYCLO [5.4.0] UNDECANES

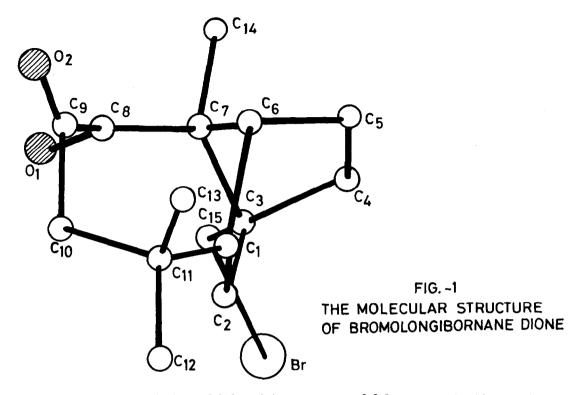
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The diversity of carbocyclic structures encountered among the sesquiterpene group of natural products has been attributed to stereoelectronically² controlled, $C^+ - \pi$ type of in vivo cyclisation of farnesyl pyrophosphate (FPP) on the enzyme surface. 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 proviso 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.



Prolonged exposure of previously reported³ ketone (II) to Jones reagent resulted in a facile, and quite unexpected exidation to a crystalline compound $C_{15}H_{21}O_{2}Br$, mp 103-4°, λ_{max}^{MeOH} 310 nm (ϵ =52), $_{2}$ $C^{=0}$ 1720 cm⁻¹; δ 1.01, 1.1 & 1.14 (3H, s, CH₃-C-), 3.58 (2H, q, J=10 Hz, -CH_-Br), 2.51 (2H, q, J=12 Hz, -C-CH_-) in 32% yield. These spectral data clearly indicated a of -diketone structure and as it was crucial to the projected work, its structure was unambiguously deduced by X-ray crystal analysis. The crystals of the diketone used for X-ray



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).⁴

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: $\mathcal{L}^{C=0}$ 1715 cm⁻¹, $\mathcal{L}^{C=CH_2}$ 885, 1645 and 3130 cm⁻¹, \mathcal{J} 0.98 (6H, s, <u>gem-dimethyl</u>), 1.02(3H, d, J=6 Hz, CH₃-C-H), 4.83(2H, broad, H₂C=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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