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BRIDGED RINGS, PART XI.[1] A NOVEL FRAGMENTATION.

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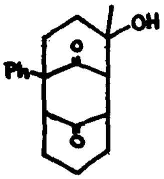
Our interest in bridged bicyclic systems together with recent reports of serendipitous syntheses of doubly bridged tricyclic molecules[2] has prompted us to attempt a rigorous synthesis and structure verification of such a molecule (1), whose conformation would be of considerable interest. The readily available[3] bicyclic ketone 2, gave one major product[4] on hydroboration, and this was oxidised to the dione 3. In view of the reliability of the Wichterle route to bridged structures,[5] the dione was alkylated with 1,3-dichloro-but-2-ene, and the product (4) was treated with 80% H_2SO_4. The resulting colourless crystalline solid [m.p. 221-2°; $C_{19}H_{22}O_3$] showed $\nu_{CO}^{CCl_4}$



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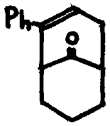

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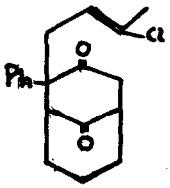
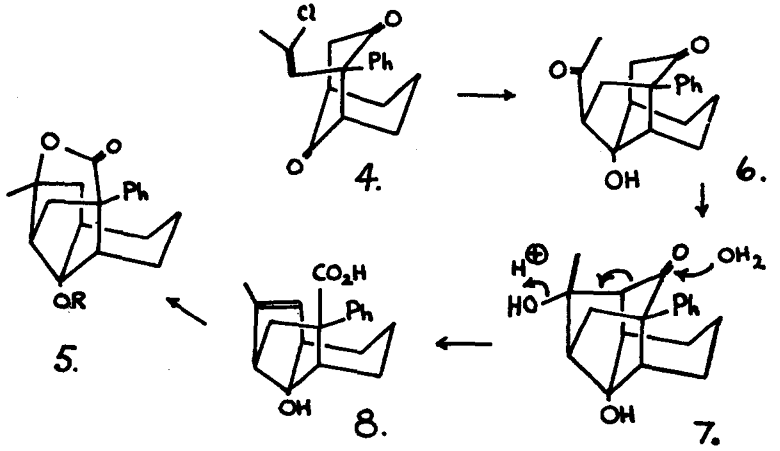


4.

1744 cm.$^{-1}$ $\nu_{CO}^{CHCl_3}$ 3595 cm.$^{-1}$ and only mono-substituted benzene absorption in the U.V. The mass-spectrum showed losses of 18 and 44 mass units from the parent peak at m/e 298. These correspond to losses of H_2O and CO_2 respectively. The n.m.r. spectrum showed a singlet CH_3 resonance at 8·49 τ (i.e., adjacent to oxygen) and (in DMSO)[6] a tertiary alcohol. It afforded a mono-acetate and a mono-formate but could not be dehydrated. It also dissolved slowly in alkali.



These data are not consistent with structure 1, and we were unable to provide a rational chemical solution to the problem. However definition of the structure as (5; R = H) has been provided by a three-dimensional X-ray analysis of crystals of the bromoacetate (5; R = $BrCH_2CO-$). The derivative crystallises in space group $P2_1/C$ with 4 molecules of $C_{21}H_{23}O_4Br$ in a cell of dimensions a = 7·16; b = 16·15; c = 17·71Å: β = 108·67°. Some 2000 intensity data were estimated visually from equi-inclination Weissenberg films. The position of the bromine atom was found from the Patterson distribution. The remainder of the structure was then elucidated by the heavy atom method and refined by Fourier and least-squares procedures on the Glasgow University KDF 9 computer. The value of R is now 14% and refinement of atomic parameters is continuing.

Mechanistically, the lactone must arise by the sequence (4) → (6) → (7) → (8) → (5) in which the bridge fission step (7 → 8) is of particular interest. It represents the appearance in a bicyclo(3.3.1)nonenone, of a fragmentation reaction previously observed[7] only in bicyclo(3,2,1)octenones. It's emergence in this particular molecule but not in simple cases[7] must be attributed to strain.

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