An Unexpected Cyclisation of an Olefinic Epoxy-ketone

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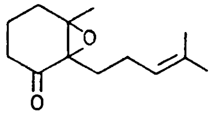
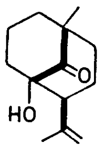
Summary Reaction of the epoxy-olefin (**1**) with Lewis acids gave the bicyclo[3.3.1]nonane derivative (**2**), possibly by an 'ene' reaction.

Following our previous successful epoxy-olefin[1] and epoxy-acetylene[2] cyclisations with compounds of the general type (**1**) we attempted to induce five-membered ring formation (5-*Exo*-Trig) by electronically biasing the double bond. Cyclisation of (**1**) with $SnCl_4$–CH_2Cl_2 at −20 °C gave (**3**) (94%), [ν_{max} ($CHCl_3$) 3490 and 1715 cm^{-1}; τ ($CDCl_3$) 9·0 (3H, s), 8·3 (3H s), 5·26 (1H, s), and 5·13 (1H, s)] whose spectroscopic properties were in accord with the expected cyclisation product (**3**), with isopropenyl group at position *). However, degradation established that this was not so. Reduction of (**3**) to the diol ($NaBH_4$) followed by HIO_4 oxidation gave the keto-aldehyde [τ ($CDCl_3$) 0·2 (1H, t), 5·0 (1H, m), 5·1 (1H, m), 7·12 (1H, dd), 8·2 (3H, br. s), and 8·96 (3H, s); ν_{max} ($CHCl_3$) 1735 cm^{-1}] which was oxidized with Jones's reagent to the acid (**4**) [ν_{max} ($CHCl_3$) 1740 and 1715 cm^{-1}; τ ($CDCl_3$) 5·1 (1H, m), 5·2 (1H, m), 7·16 (1H, dd), 8·27 (3H, br. s), and 9·0 (3H, s)]. Acid or base converted (**4**) into (**5**) [ν_{max} ($CHCl_3$) 1720 and 1670



(1)



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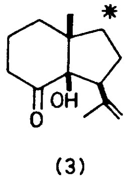

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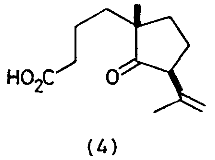

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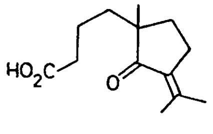

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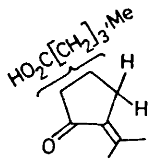
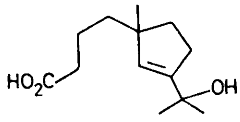


(A)



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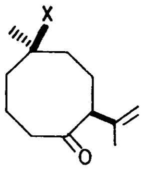
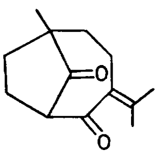


(7) X = CHO
(8) X = CO_2H



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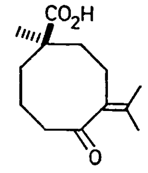

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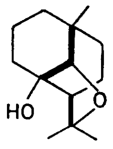

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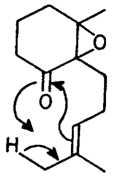

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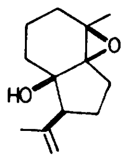

(13)

cm^{-1}; τ ($CDCl_3$) 9·0 (3H, s), 8·17 (3H, s), and 7·78 (3H, s), λ_{max} (EtOH) 253 nm (ϵ 9900)]. These data establish part structure (A) for (**5**), which was confirmed by $NaBH_4$ reduction (acid work-up) to (**6**) [τ ($CDCl_3$) 8·67 (6H, s) and 4·7 (1H, t, *J* 1·2 Hz). Some clue as to how (**3**) is formed came from the observation that (**2**) [τ ($CDCl_3$) 8·88 (3H, s), 8·25 (3H, s), 5·41 (1H, s), and 5·20 (1H, s)] is a kinetic product of reaction and can be converted into (**3**) under the conditions of reaction, or by treatment with NaOH. The structure (**2**) is secured by the following degradations. Reduction with $NaBH_4$ gave a mixture of diols which on HIO_4 oxidation yielded (**7**) [ν_{max} ($CHCl_3$) 1740 and 1705 cm^{-1}, τ ($CDCl_3$) 8·93 (3H, s), 8·25 (3H, s), 5·14 (1H, s), 5·06 (1H, s), and 0·6 (1H, s)]. Jones's oxidation of (**7**) yielded (**8**) [τ ($CDCl_3$) 8·78 (3H, s), 8·25 (3H, s), 5·11 (1H, s), and 5·04 (1H, s)], which underwent acid-catalysed Claisen condensation with toluene-*p*-sulphonic acid in benzene forming (**9**) [λ_{max} (EtOH) 253 nm (ϵ 5500); ν_{max} ($CHCl_3$) 1740 and 1685 cm^{-1}; τ ($CDCl_3$) 8·85 (3H, s), 8·32 (3H, s), and 8·15 (3H, s)]. The diketone (**9**) was smoothly hydrolysed to (**10**) [λ_{max} (EtOH) 252 nm (ϵ 1750); τ ($CDCl_3$) 8·8 (3H,s), 8·3 (6H,s)] with NaOH. The stereochemistry of (**2**) was established by conversion of the corresponding diols in part into the ether (**11**) [$Hg(OAc)_2$–H_2O then $NaBH_4$).

It is clear that (**2**) cannot be a direct product of cyclisation, but a likely precursor is (**13**) from which it can be formed by the well known epoxide-to-ketone transformation. Compound (**13**) could be formed from (**1**) by a Prins[3] or 'ene' type reaction[4] as in (**12**). Such a pathway could well be of lower energy than one forming a cyclopentylmethyl cation which is notoriously prone to rearrangement[5] when fused to other rings, *e.g.* backbone rearrangement of steroids. This would, of course, support the formation of (**13**) by a Lewis acid-catalysed 'ene' reaction rather than by a Prins which involves the intermediacy of just such a cation.

We thank the S.R.C. for support.

(*Received*, 9*th March* 1978; *Com.* 254.)

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