Some Epoxy-acetylene Cyclisations

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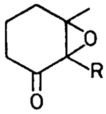
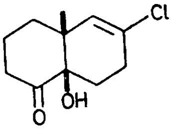
Summary Two epoxy-acetylenes have been cyclised, one containing a terminal acetylene to a decalin derivative, the other to an hydrindane derivative.

We have shown[1] that reaction of an $\alpha\beta$-epoxy ketone of type (**1**) with a Lewis acid can lead to 9-methyldecalin derivatives by cyclisation involving participation of side-chains containing mono- or di-substituted olefins or aromatic rings. We now show that acetylenic bonds can also participate in cyclisations of these types. Cyclisation of (**1**) with $BF_3.OEt_2$ or $TiCl_4$ in CH_2Cl_2 gave high yields (>90%) of (**3**) [τ($CDCl_3$) 9·05 (3H, s) and 4·35 (1H, s); ν_{max} ($CHCl_3$) 3480 and 1715 cm^{-1}]. The structure was established by reduction of (**3**) to the diol ($NaBH_4$) followed by periodate oxidation to the keto-aldehyde (**4**) [τ ($CDCl_3$) 8·9 (3H, s), 4·4 (1H, t, J 2 Hz), and 0·48 (1H, t, J 2 Hz); ν_{max} ($CHCl_3$) 1720 cm^{-1}] which on treatment with Na_2CO_3–MeOH gave (**5**) [ν_{max} ($CHCl_3$) 1680 cm^{-1}; λ_{max} (EtOH) 234 nm (ϵ 15,000)]. The electronically unbiased acetylene (**2**) cyclised to the hydrindane derivative† (**6**) (94%) [ν_{max} ($CHCl_3$) 3490 and 1715 cm^{-1}; τ ($CDCl_3$) 8·75 (3H, s) and 7·81 (3H, t, J 1·5 Hz)] with $SnCl_4$–CH_2Cl_2, the structure of which was established by degradation. Ozonolysis of (**6**) gave (**7**) [ν_{max} ($CHCl_3$) 3490 and 1750 cm^{-1}; τ 8·96 (3H, s)] demonstrating that the ring formed by cyclisation was five-membered. This was confirmed and the orientation of the side-chain indicated by reduction of (**7**) to the corresponding

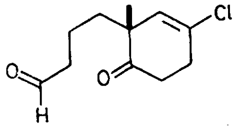


(1) R = $[CH_2]_2C{\equiv}CH$

(2) R = $[CH_2]_2C{\equiv}CMe$



(3)



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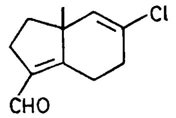

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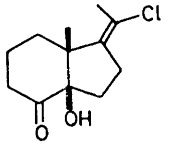

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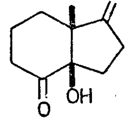

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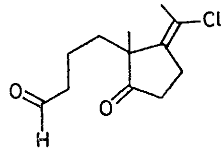

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† Professor J. E. McMurry, University of California, Santa Cruz has achieved a closely related cyclisation: personal communication.

diols ($NaBH_4$) followed by HIO_4 oxidation to (**8**) [ν_{max} ($CHCl_3$) 1750 cm^{-1}; τ ($CDCl_3$) 8·8 (3H, s), 7·8 (3H, t, *J* 1·8 Hz), and 0·3 (1H, t, *J* 1·5 Hz)]. Attempts to apply Johnson's procedure[2] of trapping the vinyl cations by vinylidene carbonate were unsuccessful in the case of (**1**) and we have no evidence for the formation of hydrindan products; (**3**) is most likely formed by a 6-*Endo*-Dig cyclisation rather than 5-*Exo*-Dig followed by rearrangement. When (**1**) was cyclised by $BF_3.OEt_2$ in pentane spectral evidence showed that formation of the vinyl fluoride and ring contraction had occurred. A combination of m.s.–g.l.c. and spectral evidence suggested that $BF_3.OEt_2$–CH_2Cl_2 cyclisation of (**2**) was forming (**6**), the corresponding vinyl fluoride, and the ring-expanded vinyl fluoride.

Ring junction stereochemistry of the cyclisation products was assigned because of the presence of an intramolecularly hydrogen bonded hydroxyl group and *E*-stereochemistry for the double bond in (**6**) followed from long-range coupling of the methyl group with the ring methylene.

These results establish that, as in carbonium ion-acetylene cyclisations,[2–4] the 5-*Exo*-Dig cyclisation[5] is favoured over 6-*Endo*-Dig when the acetylene is electronically unbiased. However, when favoured electronically the 6-*Endo*-Dig cyclisation is observed. The difference in behaviour from the corresponding olefins probably arises from the 120° approach vector which has been postulated in the case of attack on the acetylenic bond.[6]

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