Cyclisation of 1-Methyl-9-methoxy-(*E*,*Z*)-cyclonona-1,5-diene

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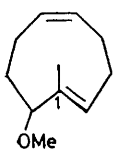
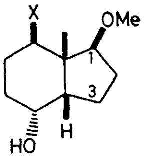
Summary The cyclisation of the title diene led to an hydrindane derivative by 1,6-bonding of the diene system and proposals are made to account for the different cyclisation paths observed in medium ring 1,5-dienes.

IN continuation of our work[1] on the cyclisation of medium-ring 1,5-dienes we now describe the cyclisation of the diene (**1**) which has been prepared by Baird.[2] Reaction of (**1**) with *N*-bromosuccinimide–acetone–water yields an hydrindane (**2**), τ 8·80 (3H, s), 6·70 (3H, s), 6·42 (1H, dd, *J* 5 and 1·5 Hz), and 5·90—6·25 (2H, m), establishing the presence of C–*Me*, –O*Me*, C*H*OMe, C*H*OH, and C*H*Br, respectively. Jones oxidation of (**2**) yielded the ketone (**4**) [ν_{max} (CCl_4) 1715 cm^{-1}; τ 8·78 (3H s), 6·72 (3H, s), 6·42

(1H, m), and 5·61 (1H, m)] which on treatment with NaOMe–MeOH gave a bicyclo[3.1.0]hexane derivative[3] (**7**) [ν_{max} (CCl_4) 1725 cm^{-1}; λ_{max} (EtOH) 226 nm (ϵ 1500); τ 8·78 (3H, s), 6·74 (3H, s), and 6·46 (1H, dd)] which exchanged 2H with NaOEt in EtOD. Reduction of (**7**) with $NaBH_4$ gave a single alcohol [τ 9·45 (1H, dd, *J* 7 and 1·5 Hz), 8·68 (3H, s), 6·7 (3H, s), 6·58 (1H, d, *J* 5Hz), and 5·42 (1H, t, *J* 8 Hz)]. Reduction of (**2**) with Li–NH_3 formed (**3**) [τ 8·95 (3H, s), 6·74 (3H, s), 6·70 (1H, m), and 6·10 (1 Hm)], which on Jones oxidation yielded (**5**) [ν_{max} (CCl_4) 1715 cm^{-1}; τ 8·94 (3H, s), λ_{max} 220 nm ϵ 300)] having 3H exchangable with NaOEt–EtOD. These data establish the part structures (A) for the ketone (**7**) and (*B*) for (**2**), which leads to two possible structures for the cyclisation product; that (**2**) is preferred to that in which the –OMe is attached to C-3 follows from the structure of the starting material. The stereochemistry is assigned on the basis of the expected 'chair-like' reacting conformation (**8**).[1] In support, the Me and Br must be *cis* to account for the formation of (**7**) with inversion of configuration at C-6.

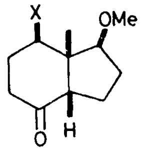


(1)



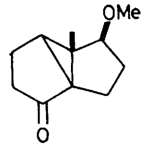
(2); X = Br

(3); X = H

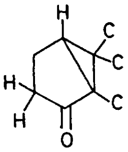


(4); X = Br

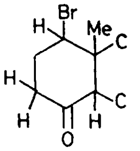
(5); X = H



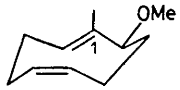
(7)



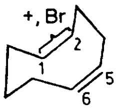
(A)



(B)



(8)



(9)

It is instructive to compare this cyclisation with that of (*Z,Z*)-cyclonona-1,5-diene[4] where 1,5-C–C bonding of the 1,5-diene system is observed, as opposed to 1,6–in the case above. The absence of other modes of ring closure in the case of (*Z,Z*)-cyclonona-1,5-diene can be understood by considering the expected conformation of the ion (**9**). 1,6-Bonding would lead to a disfavoured 'boat-like' transition state, while 2,6-bonding involves, in Baldwin's[5] nomenclature a 5-*Endo*-Trig cyclisation† which he has pointed out in his Rules for Ring Closure is sterically much less likely than the 5-*Exo*-Trig cyclisation; 1,5-bonding in (**9**) is of the latter type and leads to the observed products. In the case of the diene (**1**) C-1 is clearly the most readily generated cationic centre and bonding to C-5 or -6 are both 5-*Exo*-Trig; however, it is clear from models that C-5 is closer to C-1 and this cyclisation is observed. These results, in conjunction with the cyclisation of cyclo-octa-1,4-diene[6,7] and humulene[6] leading to annulated cyclopropanes, suggest that in medium-ring dienes the ease of trigonal cyclisation is in the order 6-*Endo* > 5-*Exo* > 4-*Exo* and 3-*Exo* > 5-*Endo*. This tentative order, taken in conjunction with expected substitution effects on double bonds and the principle of cyclisation by 'chair-like' transition states allows certain structural and stereochemical predictions to be made, in particular that 2-methylcyclonona-1,5-dienes should cyclise initially to bicyclo[5.2.0]nonanes rather than angularly methylated hydrindanes and that only 1-methyl-(*E,E*)-cyclonona-1,5-diene should yield the important angularly methylated *trans*-hydrindanes.

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† As suggested in Ref. 5 the smaller of the two rings being formed is considered.

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