Transannular Cyclisation of 1-Bromo-2,6-Dimethylcyclonona-1(*E*),5(*Z*)-dien-9-ol

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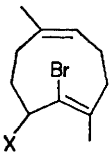
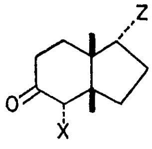
Summary Cyclisation of the title compound yields a *cis*-hydrindane in contrast to the *trans*-compounds obtained from the bisnormethyl series.

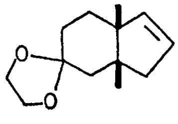
PREVIOUSLY we have shown that 9-acetoxy-1-bromocyclonona-1,5-diene can be cyclised in good yield to 5-acetoxy-1-bromotetrahydro-*trans*-indan-4(5*H*)-one with *N*-bromosuccinimide (NBS) in aqueous acetone.[1] In the



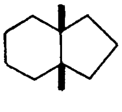
(1) X = OH
(2) X = Br



(3) X = Z = Br
(4) X = H, Z = Br
(5) X = Z = H



(6)



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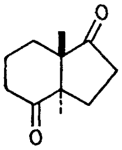

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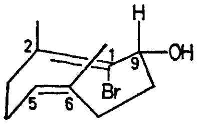

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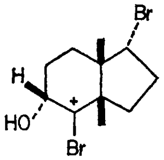

(10)

hope of extending this highly stereoselective synthesis to the synthetically more useful angularly methylated series we prepared the alcohol[2] (**1**) and treated it with NBS in aqueous acetone. Instead of the expected compound, the ketone (**3**) (30%), ν_{max} 1738 cm^{-1} (equatorial α-bromoketone), τ ($CDCl_3$) 5·36 (1H, s), 5·68 (1H, t, *J* 9 Hz), 8·76 (3H, s), and 8·78 (3H, s), was isolated. Reduction of (**3**) with Zn–AcOH gave the hydrogenolysis product (**4**), ν_{max} 1723 cm^{-1}, τ 5·72 (1H, t, *J* 9Hz), 7·83 (2H, s), 8·83 (3H, s), and 9·06 (3H, s), which exchanged four hydrogens with alkaline D_2O. Reaction with Ca in NH_3 (followed by Jones' oxidation) converted (**3**) into (**5**), τ 8·98 (3H, s) and 9·12 (3H, s). Acetalisation of (**4**) followed by dehydrobromination with KOBu^t in tetrahydrofuran gave (**6**), τ 4·51 (2H, m) and 7·88 (2H, m); decoupling experiments showed the spin system $-C-CH{=}CH-CH_2-C$ to be present. The foregoing data establish the part structures $2 \times CH_3-C-$, $CCHBr{\cdot}CH_2CH_2C$, and $CH_2CO{\cdot}CHBrC$ for (**3**) and lead to the carbon skeleton shown.† The ring junction stereochemistry was shown to be *cis* by Wolff–Kishner reduction of (**5**) to the hydrocarbon (**7**), which was not identical to the authentic *trans* hydrocarbon obtained from (**8**)[3] though the m.s. cracking patterns were identical. The stereochemistry of the bromines and the position of the secondary bromine were assigned on a mechanistic basis. Here the reacting conformation (**9**) must be different from that of the bisnormethyl series, one of the olefin units having rotated, placing its substituents on the opposite side of the ring. The fate of the cyclised carbonium ion (**10**) is also different, it being discharged by hydride migration rather than hydration, perhaps owing to steric hindrance. That the conformation (**9**) is the predominant (as well as the reacting), conformer was shown by the observation of nuclear Overhauser effects in (**1**) [Me(C-2), 18% on H(C-5)] and (**2**) [Me(C-2) 17% on H(C-5), 15% on H(C-9)]. The change in conformation between the two series is probably associated with the transannular Me–Me interaction being less severe than the corresponding Me–Br interaction and this leads to the rarely observed cyclisation of a 1,5-diene unit *via* a chair-like transition state.

We thank Dr. Reusch for experimental information, Messrs. Keyworth and Moorcroft for the decoupling and n.O.e. work, and the S.R.C. for financial assistance.

(*Received*, 21*st May* 1974; *Com.* 589.)

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† The observation that (**5**) shows two non-identical methyl signals establishes that it cannot have C_s symmetry, which excludes structures having bicyclo[3,2,1]nonane and spiro[5,3]nonane skeletons.

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[2] W. Heggie and J. K. Sutherland, *J.C.S. Chem. Comm.*, 1972, 957.

[3] P. S. Venkataramani, J. E. Karoglan, and W. Reusch, *J. Amer. Chem. Soc.*, 1971, **93**, 269.