The Stereospecific Synthesis of a *trans*-Hydrindanone

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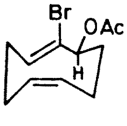
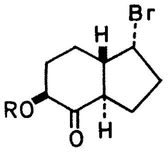
Summary Reaction of 1-bromo-9-acetoxycyclonona-1-*trans*-5-*cis*-diene with *N*-bromosuccinimide in aqueous acetone yields 1-bromo-5-acetoxy-*trans*-hydrindan-4-one.

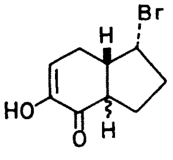
THE stereospecific synthesis of thermodynamically less stable *trans*-hydrindane derivatives has long been a problem *e.g.* in steroid synthesis,[1] and a number of indirect solutions have been described and, recently, one direct one.[2] The remarkable stereospecificity noted in the cyclisation of a number of medium-ring olefins[3] suggested that an appropriate cyclonona-1,5-diene might cyclise as required. A plausible conformation of the *cis*, *trans*-isomer (**1**) is derived simply from the known conformation of the $AgNO_3$-adduct of *cis*, *trans*-cyclodeca-1,5-diene[4] and is consistent with what is known of the n.m.r. spectra and chemistry of these compounds.



(1)



(2) R = Ac
(3) R = H



(4)

Reaction of the acetate[5] (**1**) with *N*-bromosuccinimide in aqueous acetone yielded (**2**) ν_{max} (Nujol) 1740, 1725 cm.$^{-1}$ τ (CCl_4) 4·98 (m, 1H, $W_{\frac{1}{2}}$ 18Hz), 5·50 (m, 1H, $W_{\frac{1}{2}}$ 9Hz), 7·91 (s, 3H), in 55% yield. Aqueous $NaHCO_3$–Na_2CO_3 converted (**2**) into the alcohol (**3**) [(**2**) regenerated on acetylation] which was oxidised with bismuth trioxide in acetic acid[6] to the diosphenol (**4**), λ_{max} (EtOH) 271 nm (ϵ13,000), ν_{max} (Nujol) 3400, 1680, and 1645 cm^{-1}, τ ($CDCl_3$) 4·0 (m, 1H), 5·45 (m, 1H). On treatment with ethanolic base the first recorded, λ_{max} 315 nm, rapidly changes to 362 nm. Acidification of this solution shows λ_{max} 319 nm (ϵ5500) suggesting conjugation of a double bond with the diosphenol, generated by elimination of the bromine. Reduction of (**2**) with calcium in ammonia gives an alcohol identified by g.l.c. as *trans,trans*-hydrindan-4-ol which on oxidation, equilibration of the ketone obtained with NaOMe–MeOH, followed by $LiAlH_4$ reduction gave all four isomeric hydrindan-4-ols in proportions (g.l.c.) similar to those found for reduction of the equilibrated *cis*-hydrindanone.[7] In addition the phthalate of *cis,trans*-hydrindan-4-ol[8] could be isolated from the reduction mixture obtained after equilibration. Accepting that there is no rearrangement on reduction, these results, together with the n.m.r. spectrum which indicates an equatorial acetoxyl group, establish the structure and stereochemistry of (**2**) with the exception of the stereochemistry of the bromine which is based on the expected *trans* addition to the double bond.

(*Received, November* 27*th*, 1969; *Com.* 1803.)

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