Stereospecific Cyclopropane Ring Hydrogenolysis

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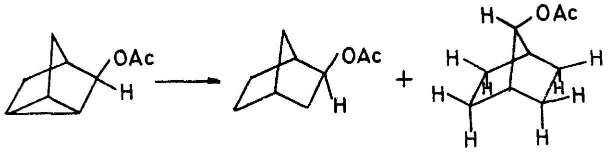
Summary Hydrogenolysis of the cyclopropane ring in 3-acetoxynortricyclene has been shown to be stereospecifically *cis*.

The ring opening of cyclopropanes by hydrogen over a metal catalyst is of wide application[1] and of particular interest to us since it is a possible step in the rearrangement of cycloalkanes over metal surfaces.[2] The one example in which the stereochemistry of hydrogenolysis of a cyclopropane ring has been established showed it to be non-stereoselective[3] over a platinum catalyst in acetic acid solution.

We have investigated the hydrogenolysis of 3-acetoxynortricyclene (**1**) over a platinum catalyst in acetic acid solution containing a small amount of perchloric acid at 80°. A mixture (32:68) of the 2-*exo*-(**2**) and 7-acetoxy-(**3**) norbornanes was obtained; no 2-*endo*-acetoxynorbornane was detected (by g.l.c. or n.m.r.). A sample of the *endo*-acetate was shown to be isomerised only slowly to the *exo*-isomer (*ca.* 5%) under the reaction conditions, indicating that the isomer ratio is almost exclusively kinetically controlled. The experiment was repeated using deuterium and the mixture of deuteriated (**2**) and (**3**) so obtained was separated by preparative g.l.c.

At 220 MHz the n.m.r. spectrum of (**3**) showed the following absorptions: τ 5·12 (s, 7-H), 7·86 (s, 1- and 4-H), 8·19 (d, *syn-exo*-H), 8·30 (s, COMe), 8·62 (d, *anti-exo*-H), 8·85 (d, *syn-endo*-H), and 9·06 (d, *anti-endo*-H) with $^{2}J_{exo-endo}$ 7·5 Hz. Assignments were made by examination of the n.m.r. spectra of specifically labelled deuterio-7-acetoxynorbornanes. *syn-exo*-Dideuterio-(**3**) was prepared by reduction ($LiAlD_4$[5]) of *syn*-norbornen-7-ol[4] and subsequent acetylation. The absorption at τ 8·19 had disappeared and was assigned to the *syn-exo*-protons while the doublet at τ 8·85 which had collapsed to a singlet was assigned to the *syn-endo*-protons. *anti-exo*-Dideuterio-(**3**) was prepared by addition of deuterium over a palladium catalyst to 7-*anti*-acetoxynorbornene[5] and its spectrum showed no absorption at τ 8·62 and a singlet at τ 9·06. Further, addition of deuterium to 7-acetoxynorbornadiene over a platinum catalyst gave a compound which showed singlets at τ 8·19 and 9·06 with smaller singlets at τ 8·62 and 8·85 suggesting that *exo*-addition to the *anti*-olefinic bond and *endo*-addition to the *syn*-olefinic bond were predominant, in agreement with previous suggestions.[6] Integration of the spectrum of deuteriated (**3**) obtained by deuteriolysis of (**1**) now showed only single protons for the *syn*- and *anti*-*endo*-absorptions.† Thus hydrogenolysis of the cyclopropane ring in 7-acetoxynortricyclene involves predominant (>90%) *cis*-hydrogen addition from the outer edge of the cyclopropane ring. This result thus parallels the stereochemistry of hydrogenation of many olefins[1] and provides an interesting contrast with the previous, non-specific, reaction.[3]



(1) (2) (3)

It was not possible to elucidate fully the stereochemistry of deuterium incorporation into the 2-*exo*-acetate (**2**) because of the complexity of its n.m.r. spectrum. However, the absorption due to the 2-*endo*-proton in the deuteriated compound was modified in a manner consistent with loss of the large $^{3}J_{endo-endo}$ coupling.[7] This observation is in agreement with the formation of 3,5-di-*endo*-deuterio-2-acetoxynorbornane, as would be predicted for a stereospecific deuterium incorporation similar to that observed in (**3**).

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† The evidence does not exclude the formation of 2,5-di-*endo*-deuterio-7-acetoxynorbornane. However, formation of this isomer must involve a highly improbable stereospecific rearrangement and incorporation of deuterium is almost certainly into the 2,6-*endo* positions.

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