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THE EXCHANGE OF NORBORNANE WITH DEUTERIUM ON A PALLADIUM SURFACE

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The chemistry of norbornane derivatives is dominated by exo-attack by reagents.[1,6] Apart from the finding[2] that 2,3-di-substituted norbornenes yield largely the cis-endo-products in hydrogenation on Adams platinum, there is a dearth of results on the relative accessibility of catalyst surface sites to geometrically different positions in this structure.

The heterogeneous exchange reaction between norbornane and deuterium has been partially studied by Burwell and co-workers[3] who showed that on Pd a maximum incorporation of two deuterium atoms results from each sojourn on the surface. These are associated with C-2 and C-3. The position of these exchanged atoms (whether exo or endo or both) has not to our knowledge been determined. A study of the N.M.R. spectrum of exchanged norbornane to be described shows that the exo-positions are involved almost exclusively.

A deuterium-norbornane mixture was admitted onto a Pd film laid at 0°C in the manner of Kemball[4] and the reaction monitored by a mass spectrometer. As found by Burwell, the only initial products were d_1- and d_2-norbornane. The reaction was, however, allowed to proceed around 200° until only ~20% of the norbornane remained unexchanged, that is until a considerable fraction of the reactant had spent several sojourns at the surface. The hydrocarbon was then 'trapped' and removed for N.M.R. analysis.

The N.M.R. spectrum of norbornane (Fig. 1A *cf*. ref. 5) shows in order of increasing field strength a peak of relative intensity 2.0 ascribed to the two tertiary bridgehead hydrogens, a doublet (resulting from splitting by the axial protons) ascribed to the 4 equatorial (exo) hydrogens with relative intensity 4.0 followed closely by an irregular peak of intensity 6.0 attributed to overlap of the two bridge hydrogens with the doublet from the four axial hydrogen atoms.

The N.M.R. spectrum of our product (Fig. 1B) showed that the ratio of endo + bridgehead hydrogens to bridge hydrogen was unchanged at 3:1. However the ratio of exo-hydrogens to bridge hydrogens had decreased by 50±5% - showing that only exo-hydrogens had been exchanged

The relative amounts of individual norbornanes from mass spectrometry (after correction for fragmentation and isotope abundance) were as follows:

d_0	d_1	d_2	d_3	d_4	d_5
21.7	12.7	22.3	19.8	16.2	7.3

The presence of d_5 shows that some hydrogens other than exo can exchange. As there are 6 endo + bridgehead hydrogens on average only 1.2% of these hydrogens have been exchanged - a percentage too small to have been detected in the N.M.R. measurements. It can be calculated from the above distribution pattern, assuming only exo-exchange occurs, that the average number of exo-hydrogens exchanged is 52.5% - in excellent agreement with the 50±5% calculated from the N.M.R. spectrum.

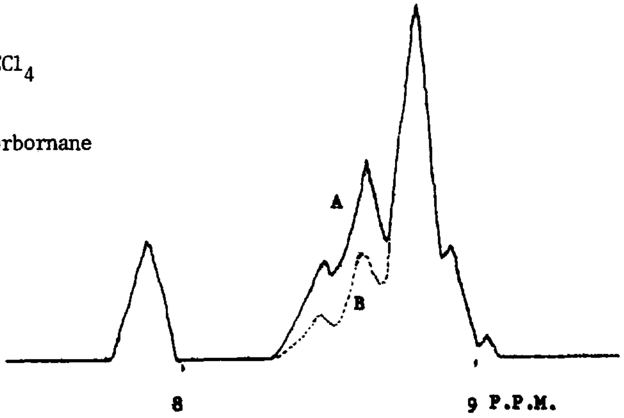
Further work is planned involving blockage towards exo-attack by interposing bulky substituents at the 7 (and 7') positions.

Fig. 1

60 MHz CCl_4

A Norbornane

B Exchanged norbornane



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