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THE STEREOCHEMISTRY AND MECHANISM OF HYDROGENOLYSIS OF THE CYCLOPROPANE RINGS IN SOME PROPELLANES

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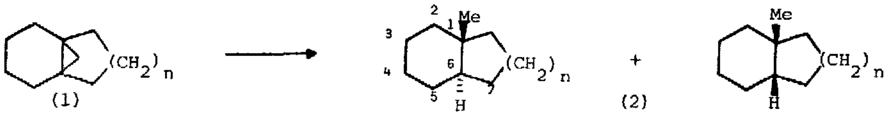
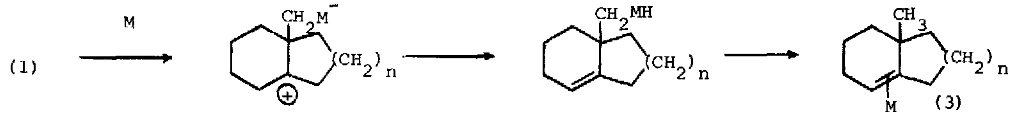
The stereochemistry and mechanism of hydrogenolysis of cyclopropane rings has been the subject of much recent study[1-4] since Schleyer and Majerksi[1] reported that reaction of tricyclo[4,4,1,0]-undecane (1, n = 2) with hydrogen over platinum in acetic acid solution gave almost equal amounts of the cis- and trans-methyldecalins (2, n = 2). We have confirmed these results for reaction in acetic acid solution and also shown that similar product ratios are obtained (50:50±10%) when (1, n = 2) is passed in a stream of hydrogen over a variety of metal catalysts (palladium and platinum, 2-10% on pumice and silica) over a range of temperatures (55-200°). We now report that in contrast reaction of tricyclo[4,3,1,0]decane (1, n = 1) over a similar range of catalysts gave a high proportion of the cis-isomer (95 cis to 5 trans ±5%). The stereoselectivity displayed in these product ratios thus parallels that previously reported for hydrogenation of the corresponding bridgehead alkenes.[5] Similar surface adsorbed species for the two sets of reactions could arise via an initial metal insertion into a cyclopropane bond leading to an adsorbed alkene species (3). The proposal that metal insertion may compete with direct hydrogen transfer from the metal surface has been made previously to account for the products of hydrogenolysis of some nortricyclenes.[6] In addition many examples of the reactions of metal ions with strained ring systems are known.[7]





The participation of adsorbed alkene species resembling (3) must obviously involve elimination-addition of hydrogen atoms at C_5 and C_7 as well as addition of hydrogens to C_6 and the methyl carbon. In addition further exchange of hydrogens could occur at C_4 and/or C_8 by the well known α,β-exchange process[8] once an intermediate resembling an adsorbed alkene had been formed. Evidence that this does occur came from reactions of the propellanes with deuterium. Reaction of the tricyclodecane (1, n = 1) with deuterium (20 cm^3 min^{-1}) at 145° over 2% palladium on silica gave a high conversion to the methyl hydrindanes in which the cis-isomer predominated (> 95%). The mass spectrum of the product showed a distribution of deuterium containing species from $C_{10}H_{16}D_2$ to $C_{10}H_8D_{10}$ with a maximum at $C_{10}H_{12}D_6$. The ^{13}C spectrum of the deuterated sample was compared with that of cis-1-methylbicyclo[4,3,0]nonane. In addition to the virtual disappearance of the peak assigned to C-6* (at 45.1) significant reductions in intensity occurred in peaks assigned to C-7 (ca. 45%) at 29.1 and to C-8 (ca. 30%) at 20.7 ppm. Triplets of low intensity appeared at similar chemical shifts to those of C-7 and C-8 suggesting the presence of $>$CHD in addition to $>CH_2$ and probably $>CD_2$ species. The absorption at 26.85 ppm which was assigned to both C-5 and the methyl group also decreased (by ca. 50%) but the other peaks, i.e. due to C-2, C-3, C-4 and C-9 retained their intensity relative to that of the quaternary carbon C-1. No incorporation of deuterium occurred when cis-(2, n = 1) was treated with deuterium under the same conditions, neither did the corresponding trans-compound incorporate deuterium nor isomerise. Similar trends were observed in reactions of deuterium with tricycloundecane (1, n = 2).

These results contrast with the reaction of deuterium with 3-acetoxynortricycle over platinum in acetic acid solution where only two deuterium atoms were introduced.[2] Thus metal insertion is only dominant where the ring system is highly strained and/or where the availability of surface hydrogen is limited.[6]

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* Details of the full ^{13}C spectral assignment, including the preparation of specifically deuterated model compounds, will be reported elsewhere; K. R. Gooding, W. R. Jackson, C. F. Pincombe and D. Rash, Aust. J. Chem., submitted for publication.