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SPECIFIC DEUTERATION OF SOME UNSATURATED COMPOUNDS

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Tristriphenylphosphine rhodium chloride was introduced as a soluble hydrogenation catalyst[1] and as a carrier of molecular hydrogen would be expected to produce specific cis deuteration of double bonds. We have shown previously[2] that although subject to considerable steric hindrance, it does hydrogenate many double bonds, and from mass spectral evidence when deuterium is employed, two atoms are added to a double bond without "scrambling". For example, methyl oleate gives a dideutero-derivative (stearic ester), m/e 300 as the parent peak. A number of examples in the steroid series include the addition of 2D only to the 1-double bond in a 1,4-dienone, the 16-double bond in pregnadienolone acetate and the 5-double bond in ergosterol.[2] In the last case it can readily be shown by standard methods that the A - B ring-junction is trans, indicating a 5α-D, but the stereo-chemistry of the 6-D could not be inferred because of the complexity of the n.m.r. spectrum due to the presence of the side-chain double bond.

By application of this reaction to 22-dihydroergosteryl acetate, we have now shown the addition to give a 6α-D, confirming the expectation of stereospecific cis addition. The n.m.r. spectrum of the resulting 5α, 6-d_2-ergost-7-en-3β-ol, 3β acetate (I) shows a clear singlet at τ 4.88 due to the proton at C-7, which is not coupled with the proton at C-6. Examination of Dreiding models shows that the dihedral angle between $H_{6\beta}$ and H_7 is close to 90°, for

which a coupling constant $J_{6\beta, 7} \cong 0^{\circ}$ would be expected, whereas a 6α-proton with a dihedral angle $\cong 30^{\circ}$ would be expected to show some coupling. The band due to this proton in the spectrum of the corresponding dihydro-compound is much broader with evidence of splitting as expected.

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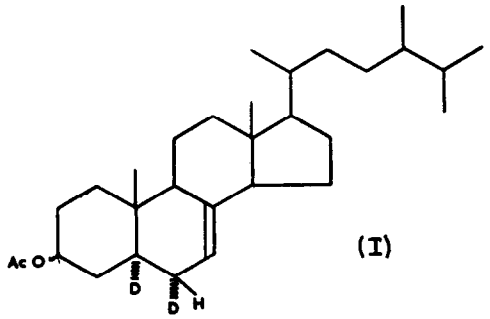

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