Isomerization of a Steroid Borane

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THE hydration of olefinic double bonds by hydroboration[1] has been applied to a number of unsaturated steroids.[2] The thermal isomerization of organoboranes has been carried out with boranes derived from aliphatic, and mono- and bi-cyclic olefins such as methylcyclohexane and α-pinene.[3]

Brown *et al.*,[4] has shown that the boron atom during isomerization is capable of moving out of a ring into an exocyclic position. It has not been shown so far what happens during isomerization in the case of a fused ring system such as a steroid.

In order to see if the boron atom of an organoborane will migrate past a ring juncture from one ring to another, cholest-5-ene was chosen. The compound was treated with gaseous diborane in diglyme, and the reaction mixture heated under reflux in a nitrogen atmosphere for 24 hr.; the product was then converted into alcohols by treatment with alkaline hydrogen peroxide.[5] The resulting mixture of cholestanols was analyzed by thin-layer and by gas-liquid chromatography.

Hydroboration, without isomerization of cholest-5-ene is known to give about 60% 5α-cholestan-6α-ol and 30% 5β-cholestan-6β-ol.[6] After thermal isomerization the mixture had the following composition:

5α-cholestan-2α-ol	29%	5α-cholestan-6α-ol	20%
5α-cholestan-3β-ol	17%	5α-cholestan-7β-ol	8%
5α-cholestan-4α-ol	15%		

5β-cholestan-6β-ol, 5β-cholestan-4β-ol, and two other unidentified steroids in trace amounts.

The boron atom in the organoborane derived from cholest-5-ene therefore prefers to migrate into ring A from ring B of the steroid, and to accommodate itself in an equatorial position. This conformational preference is in agreement with the results of Brown[4] on the isomeric distribution of the boron within the cyclohexane ring.

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