

Isomerization of a Steroid Borane

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THE hydration of olefinic double bonds by hydroboration¹ 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% 5 α -cholestan-6 α -ol and 30% 5 β -cholestan-6 β -ol.⁶ After thermal isomerization the mixture had the following composition:

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

5 β -cholestan-6 β -ol, 5 β -cholestan-4 β -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 Brown⁴ on the isomeric distribution of the boron within the cyclohexane ring.

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¹ H. C. Brown, "Hydroboration", W. A. Benjamin, New York, 1962.

² M. Nussim, Y. Mazur, and F. Sondheimer, *J. Org. Chem.*, 1964, **29**, 1120, 1131.

³ Ref. 1, p. 136.

⁴ H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, 1967, **89**, 561.

⁵ H. C. Brown and B. C. Subba Rao, *J. Amer. Chem. Soc.*, 1959, **81**, 6423, 6428.

⁶ D. Neville Jones and D. E. Kline, *J. Chem. Soc. (C)*, 1966, 846.