Thermal Isomerizations of Steroidal Boranes: Isomerizations at the Junction of the Hydrindanic Steroidal System

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Summary Thermal isomerizations of steroidal boranes provides a fast and simple synthesis of *cis*- and *trans*-hydrindanic steroidal systems.

Isomerizations of steroidal boranes are useful synthetically, especially in reactions at the junction of the steroidal hydrindanic system. Hydroboration with B_2H_6 of the steroidal $\Delta^{13,14}$ olefin (I) in diglyme at room temperature afforded a mixture of the steroidal boranes (II), (III), and (IV) characterized, after oxidation with H_2O_2 and acetylation, respectively, as compounds (V), (VI), and (VII);† heating at 50—60° of the hydroboration mixture afford primarily (68%) the steroidal borane (II). If the heating is carried at higher temperature a new borane (VIII) is

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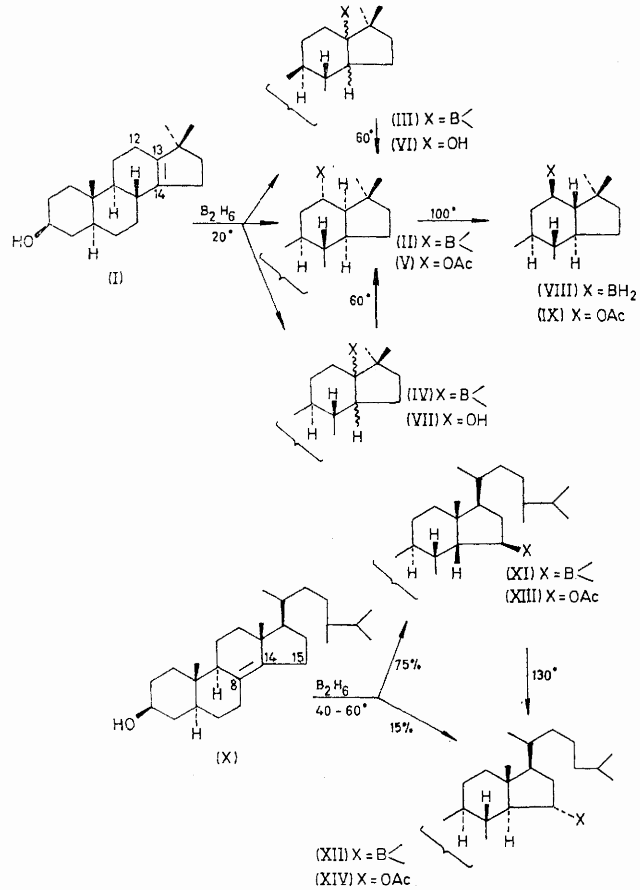
† The structures of the compounds derived from (I) were established spectroscopically (n.m.r. data and application of the octant rule); compounds derived from (X) were identified by comparison with authentic samples.

obtained, characterized as acetyl derivative (IX); compound (VIII) is the main product at 75°.



The steroidal olefin (I) is therefore selectively hydroborated at C-13 and the borane group, on subsequent mild heating, migrates to C-12 furnishing exclusively the *cis*-junction product (II). At higher temperatures (II) is converted in good yield (67%) into the *trans*-13,14-isomer (VIII).

The formation at low temperatures of the 12α-boron compound (II) can be accounted for in terms of kinetic control; migration to C-12 of the boron atom from the α-face of the molecule clearly involves less steric hindrance.

The thermal conversion of (II) into (VIII) which follows is sterically unfavoured, but the product (VIII) has greater thermodynamic stability. Hydrindanic steroidal structures with a *trans*-13,14-ring junction and 17β-alkyl-substituents are known to be more stable.[1]

We have also studied the hydroboration of the $\Delta^{8,14}$-compound (X), which has been reported[2] to be inert to hydroboration. We find that, at 40—60°, compound (X) is hydroborated extensively and two steroidal boranes (XI) and (XII) are obtained (75 and 15%, respectively), characterized as their acetyl derivatives (XIII) and (XIV). If the mixture of (XI) and (XII) is heated at 130°, formation of compound (XII) is favoured (73% yield). This is in agreement with previous observations that the *trans*-boro-derivative (XII) should predominate at higher temperatures. Hence, by choice of reaction temperature it is possible to obtain 15α- as well as 15β-derivatives with the 13,14-ring-junction respectively *trans* and *cis*. We also conclude that, in general, steroidal boron derivatives with a 13,14-*trans*-junction in the hydrindanic system are formed exclusively at higher temperatures.

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