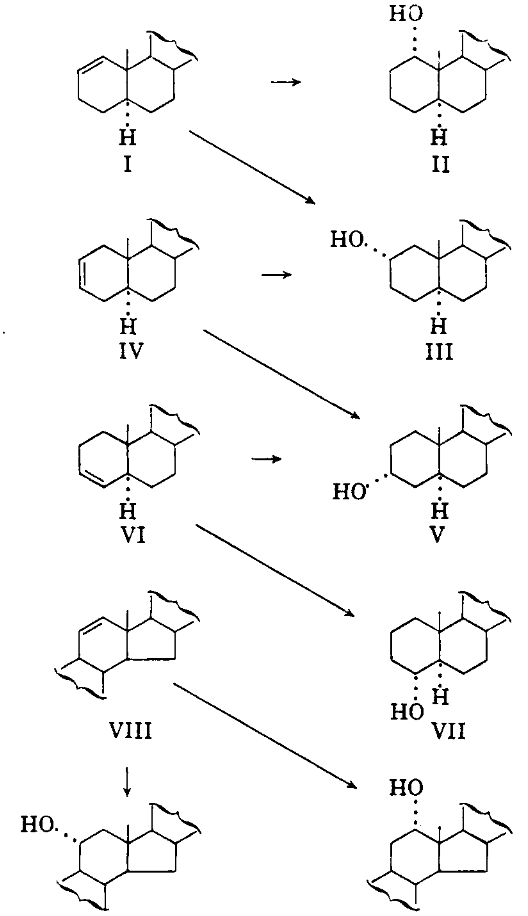
tion) afforded 35% of cholestan-2α-ol (III) (m.p. 180–182°, identified with the above-described compound) and 45% of cholestan-3α-ol (V) (m.p. 187–188°, $[\alpha]_D$ +24°; acetate: m.p. 97–98°, $[\alpha]_D$ +28°; ketone: m.p. 127–128°, $[\alpha]_D$ +40°, identified with an authentic sample). Δ^3-Cholestene (VI) by method a[4] yielded 40% of cholestan-3α-ol (V) (m.p. 187–188°, identified with the compound obtained above) and 45% of cholestan-4α-ol (VII) (m.p. 188–189°, $[\alpha]_D$ +3°; acetate: m.p. 110–112°, $[\alpha]_D$ +15°; ketone: m.p. 99–100°, $[\alpha]_D$ +30°). 5α-25D-Δ^{11}-Spirosten-3β-ol acetate (VIII) by method b (in tetrahydrofuran solution) followed by saponification gave 40% of 5α-25D-spirostane-3β,11α-diol (IX) (m.p. 216–218°, $[\alpha]_D$ −68°, identified with an authentic sample; diacetate: m.p. 175–177°) and 40% of 5α-25D-spirostane-3β,12α-diol (X) (m.p. 214–217°, $[\alpha]_D$ −30°[7]; diacetate: m.p. 153–155°, $[\alpha]_D$ −12°[7])



Very recently Brown and Zweifel[8] have shown that hydroboration of acyclic olefins with the sterically hindered bis-3-methyl-2-butylborane results in greater steric control than if diborane is employed. Consequently we have investigated the hydration of several steroidal 1,2-disubstituted ethylenes by use of this reagent and subsequent oxidation. Reaction of Δ^1-cholestene (I) with bis-3-methyl-2-butylborane (prepared by hydroboration of 2-methyl-2-butene either with lithium aluminum hydride and boron trifluoride in ether[1b,2] or with sodium borohydride and boron trifluoride in diglyme[8]) followed by oxidation with hydrogen peroxide indeed yielded 75% of cholestan-2α-ol (III), the less hindered isomer, and no detectable amount of cholestan-1α-ol (II). On the other hand no very significant change from the previous results were observed when Δ^2-cholestene (IV) and Δ^3-cholestene (VI) were allowed to react with bis-3-methyl-2-butylborane, the former giving 35% of cholestan-2α-ol (III) and 45% of cholestan-3α-ol (V), while the latter gave 45% of cholestan-3α-ol (V) and 35% of cholestan-4α-ol (VII).

A typical experimental procedure for carrying out the reaction of Δ^1-cholestene (I) with bis-3-methyl-2-butylborane follows.

A solution of 0.50 g. (13.2 mmoles) of lithium aluminum hydride in 30 cc. of dry ether was added dropwise during 20 min. to a stirred solution containing 2.47 g. (35.3 mmoles) of 2-methyl-2-butene and 2.50 g. (17.6 mmoles) of boron trifluoride etherate in 40 cc. of ether, with ice-cooling under nitrogen. After an additional 1 hr. at 0°, a solution of 0.50 g. (1.35 mmoles) of Δ^1-cholestene (I) (m.p. 69–70°, $[\alpha]_D$ +14°) in 30 cc. of ether was added during 5 min. and the mixture was allowed to stand for 4 hr. without further cooling. It was then treated with a saturated sodium sulfate solution and solid sodium sulfate, and was filtered and evaporated. The residue dissolved in 20 cc. of tetrahydrofuran was oxidized with 10 cc. of 30% hydrogen peroxide and 15 cc. of 10% aqueous sodium hydroxide for 1 hr. at 0°. Isolation with ether followed by chromatography on alumina and crystallization from methanol yielded 0.39 g. (74%) of cholestan-2α-ol (III), m.p. 178–180°, $[\alpha]_D$ +27°. Almost identical results were obtained when the hydroboration of 2-methyl-2-butene was carried out with sodium borohydride and boron trifluoride in diethyleneglycol dimethyl ether.[8]

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Protonolysis and Deuterolysis of Tri-2-norbornylborane—Evidence for the Retention of Configuration in the Protonolysis of Organoboranes

Sir:

The hydroboration of olefins, followed by protonolysis with carboxylic acids, provides a convenient

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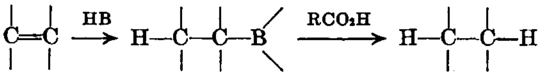
(7) In acetone.

(8) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, 82, 3222 (1960).

procedure for the conversion of alkenes into the corresponding alkanes.[1]

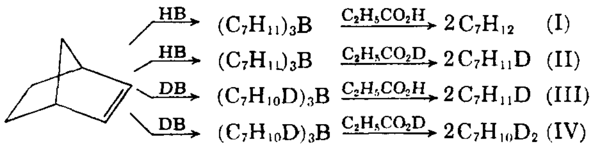


$$\mathrm{C{=}C} \xrightarrow{\mathrm{HB}} \mathrm{H{-}C{-}C{-}B} \xrightarrow{\mathrm{RCO_2H}} \mathrm{H{-}C{-}C{-}H}$$

A knowledge of the stereochemistry of the protonlysis stage, similar to that now available for the hydrogen peroxide oxidation, would permit the stereospecific synthesis of alkanes and deuteroalkanes. It appeared that an NMR examination of the mono- and dideuteronorbornanes synthesized *via* hydroboration would provide evidence on this point.

The hydroboration of norbornene readily produces the corresponding organoborane (*exo*[2]) and protonlysis of two of the three alkyl groups is readily achieved with propionic acid, forming norbornane, b.p. 104–105° at 747 mm., m.p. 85.5–87°. Oxidation of the reaction residue with alkaline hydrogen peroxide converted the third group into *exo*-norborneol, m.p. 124–125°.

The deutero derivatives were prepared through corresponding reactions involving hydroboration with B_2D_6 and protonolysis with both propionic acid and deuterated propionic acid.



$$\xrightarrow{\mathrm{HB}} (\mathrm{C_7H_{11}})_3\mathrm{B} \xrightarrow{\mathrm{C_2H_5CO_2H}} 2\,\mathrm{C_7H_{12}} \quad (\mathrm{I})$$
$$\xrightarrow{\mathrm{HB}} (\mathrm{C_7H_{11}})_3\mathrm{B} \xrightarrow{\mathrm{C_2H_5CO_2D}} 2\,\mathrm{C_7H_{11}D} \quad (\mathrm{II})$$
$$\xrightarrow{\mathrm{DB}} (\mathrm{C_7H_{10}D})_3\mathrm{B} \xrightarrow{\mathrm{C_2H_5CO_2H}} 2\,\mathrm{C_7H_{11}D} \quad (\mathrm{III})$$
$$\xrightarrow{\mathrm{DB}} (\mathrm{C_7H_{10}D})_3\mathrm{B} \xrightarrow{\mathrm{C_2H_5CO_2D}} 2\,\mathrm{C_7H_{10}D_2} \quad (\mathrm{IV})$$

The NMR spectrum (Varian, 60 Mc spectrometer) of the norbornane (I) indicated in order of increasing field strength a peak of relative intensity 2.0, ascribed to the two tertiary bridgehead hydrogen atoms, a doublet (resulting from splitting by the axial protons) ascribed to the four equatorial (*exo*) hydrogen atoms with a relative intensity of 4.0, followed closely by an irregular peak of intensity 6.4, attributed to overlap of the two bridge hydrogen atoms with the doublet from the four axial hydrogens.[3]

The NMR spectra of the two monodeuterated norbornanes (II and III) were identical, with the relative intensity of the equatorial doublet decreased from 4.0 to 3.0. Finally, in the case of the dideuterated derivative, IV, the relative intensity of the equatorial hydrogen doublet decreased to 2.0, the relative intensities of the three peaks changing from the 2.0:4.0:6.4 value for norbornane (I) to 2.0:2.0:6.2 for the dideuteronorbornane (IV).

These results are consistent both with the pure *cis* addition of the hydrogen-boron bond from the less hindered direction (*exo*[2]) and with the retention of configuration in the protonolysis of the organoborane.

It is not possible to generalize rigorously from the present single result with the norbornane system to all other organoboranes. However, the stereochemistry of the alkaline hydrogen peroxide oxidation has been demonstrated to proceed with retention in many systems.[2,4,5] In this reaction the organoborane from norbornene behaves the same stereochemically as all other monocyclic and acyclic systems.[2] The protonolysis of the vinylboranes from the hydroboration of acetylenes proceeds with retention of configuration.[6] Finally, numerous electrophilic substitution reactions of organomercurials have been demonstrated to proceed with retention of configuration.[7] Consequently, it appears reasonable that the protonolysis of organoboranes may proceed quite generally with retention of configuration.

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[2] H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **81**, 247 (1959).

[3] It is generally accepted that the proton magnetic resonance spectra of the axial hydrogens of cyclohexane derivatives occur at higher fields than those for equatorial hydrogens: R. V. Lemieux, R. K. Kulling, H. J. Bernstein, and W. G. Schneider, *J. Am. Chem. Soc.*, **80**, 6098 (1958); F. R. Jensen, D. S. Noyce, C. H. Sederholm, and A. J. Berlin, *J. Am. Chem Soc.*, **82**, 1256 (1960).

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Synchronous Decarboxylation and Dehydration

Sir:

We wish to report evidence showing that β-*p*-methoxyphenyl-β-hydroxypropionic acid (I) undergoes facile, synchronous decarboxylation and dehydration in dilute acidic solution.

Upon heating in dilute (0.1*N*) sulfuric acid at 45°, I loses carbon dioxide in nearly quantitative yield.

From the decarboxylative dehydration, *p*-methoxystyrene has been isolated (largely as a colorless waxy polymer) along with a small amount of anis-