nyl-3-buten-2-ol but in lesser amount. The ratio of products for 3 substitution was carbonyl/alcohol = 0.4 in our case vs. 0.8 in theirs. In the reactions of 3-methyl-2-buten-1-ol, unsaturated alcohols were also found as products and this additional information is noted in Table II. Case A products, therefore, appear to become significant with certain structures. However, case B products are favored under our conditions and we have obtained carbonyl compounds as major products from some unsaturated alcohols in which the double bond and hydroxyl function are well separated, e.g., 4-methyl-4-penten-1-ol. Even 1-decen-10-ol gave significant amounts of aldehyde products. We will report further on the reactions of nonallylic unsaturated alcohols in a subsequent paper.

Experimental Section

Reagents, catalysts, and solvents were commercial products and were used without purification.

Reactions were carried out under a nitrogen blanket in a flask equipped with a serum cap for the removal of GC samples. When conversion reached 100% or ceased, the reaction mixture was stirred with a five- to tenfold excess of water and extracted with toluene. The products were then distilled from the toluene extract or separated by preparative GC. In some cases, yields were obtained by GC during or at the end of the experiment, by the addition of an internal standard. A typical example follows. Deviations from this procedure are noted in the Results section.

3-Phenyl-2-methylpropanal. $PdCl_2$ (0.80 g) was dissolved in 200 ml of hexamethylphosphoramide at 140° and cooled, and 79 g of bromobenzene, 54 g of methallyl alcohol and 50 g of sodium bicarbonate added. The mixture was heated under nitrogen while stirring and monitored by GC. After 3 hr the reaction mixture was cooled, 200 ml of toluene was added, and the mixture was extracted twice with 1 l. of water. The toluene solution was then evaporated to give 63 g of liquid which was distilled under nitrogen at 10 mm pressure to give 53 g of 3-phenyl-2-methylpropanal (72% yield).

(1) Conversions and yields may frequently be improved by the addition of triphenylphosphine, e.g., 2.4 g (2 mol/mol $PdCl_2$).

(2) Rates may be increased by the addition of a small amount of a tertiary amine, e.g., 1 g of triethylamine.

(3) Satisfactory results have also been obtained in some cases when the concentration of the palladium catalyst was decreased by a factor of 0.2 and even 0.04.

Registry No.—Iodobenzene, 591-50-4; bromobenzene, 108-86-1; 3-phenylbutanal, 16251-77-7; 2-phenylbutanal, 2439-43-2; 3-phenyl-2-butanone, 769-59-5; 2-methyl-4-phenyl-3-buten-2-ol, 25625-21-2.

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Hydroboration of Monoterpene Alcohols

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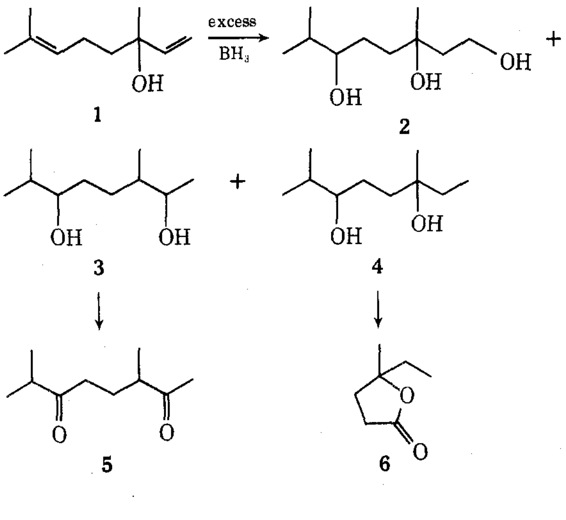
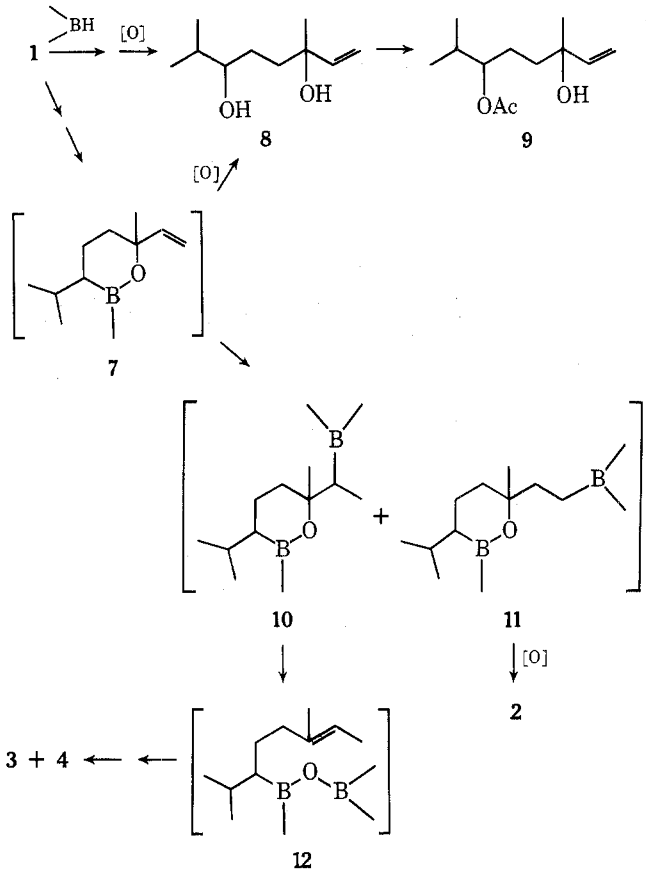
The reaction of linalool (1) with excess borane in tetrahydrofuran at ambient temperature affords 3,7-dimethyl-2,6-octanediol (3) and 3,7-dimethyl-1,3,6-octanetriol (2), while treatment of 1 with 0.67 equiv of borane produces 3,7-dimethyl-1-octen-3,6-diol (8). Hydroboration of linalool (1) with disiamylborane yields 3,7-dimethyl-6-octen-1,3-diol (13). The reaction of geraniol (15) or citral (14) with borane in THF yields after oxidation a mixture of 2 and 3,7-dimethyl-1,2,6-octanetriol (18). Distillation of the intermediary boranes yields 22% of 8-isopropyl-5-methyl-1-bora-2-oxabicyclo[3.3.0]octane (16). The remainder of the organoboranes undergo β-elimination upon heating to afford, after oxidation, 3,7-dimethyl-1-octen-6-ol (20) and 3,7-dimethyl-1,6-octanediol (21).

Cornforth[1] has reported that the hydroboration–oxidation of linalool (1) results in the formation of 30% of an unidentified diol in addition to 60% of 3,7-dimethyl-1,3,6-octanetriol (2), even when an excess of borane is used. We have confirmed these observations using a 50% excess of borane in THF and find that the diol is a 4:1 mixture of 3,7-dimethyl-2,6-octanediol (3) and 3,7-dimethyl-3,6-octanediol (4). Jones oxidation of the diol mixture afforded 3,7-dimethyl-2,6-octanedione (5) and 4-methyl-4-hydroxyhexanoic acid lactone (6).[2]

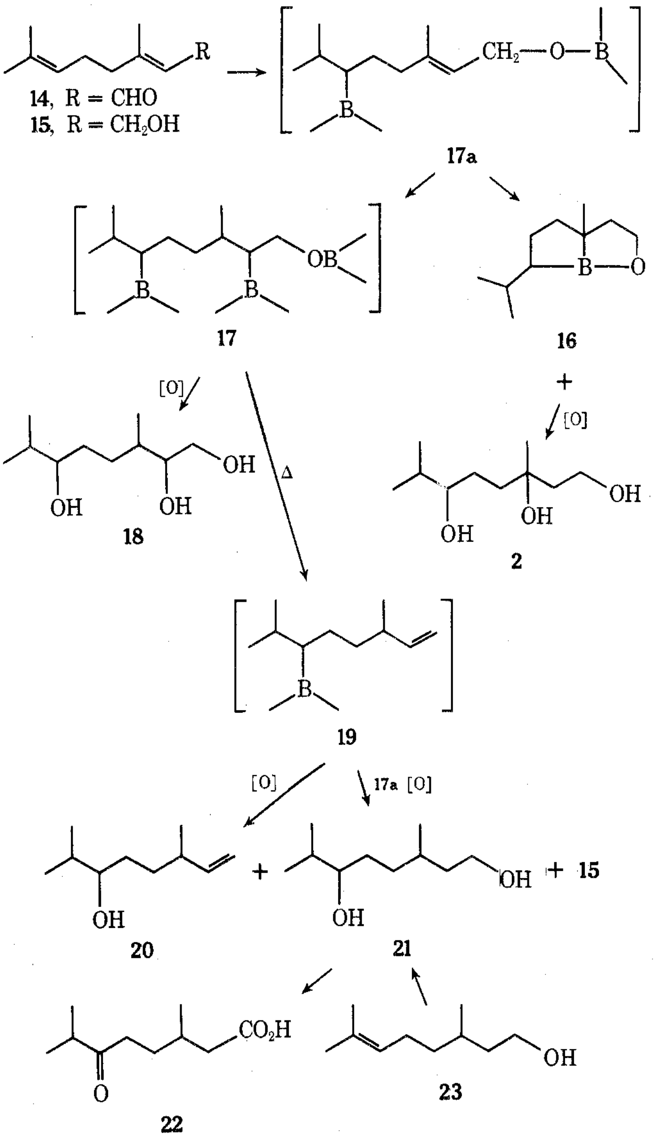


In order to gain an insight into the formation of diols 3 and 4, linalool (1) was treated with 0.67 equiv of borane. Oxidation afforded recovered linalool (28%), triol 2 (9%), and 34% of 3,7-dimethyl-1-octene-3,6-diol (8) which was converted to the known monoacetate 9[3] using acetic anhydride and pyridine. The formation of the 3,6-diol 8 to the exclusion of the 1,3-diol 13 is most likely the result of ini-

Scheme I



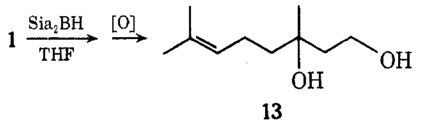
Scheme II



tial reaction of borane with the alcohol group[4] to afford an alkoxyborane which chooses to react in an intramolecular fashion to form oxaborinane **7**, which upon oxidation is converted to diol **8**.

In the presence of excess borane, intermediate **7** is apparently attacked at C-2 and C-1 to give **10**[5] and **11**. Borane **11** is stable and leads ultimately to triol **2**. The β-substituted organoborane **10** presumably undergoes a facile 1,2-elimination to **12**.[6] Reaction of **12** with more borane (boron attack at the secondary carbon atom), or intramolecular B-H addition permitting attachment of boron at the tertiary carbon,[7] leads ultimately to **3** and **4**, respectively (Scheme I).

In contrast to the above-mentioned results, the reaction of linalool (**1**) with the more sterically hindered disiamylborane[9] occurs exclusively at the C-1 position of the vinyl group to afford a 66% yield of 3,7-dimethyl-6-octene-1,3-diol (**13**).



13

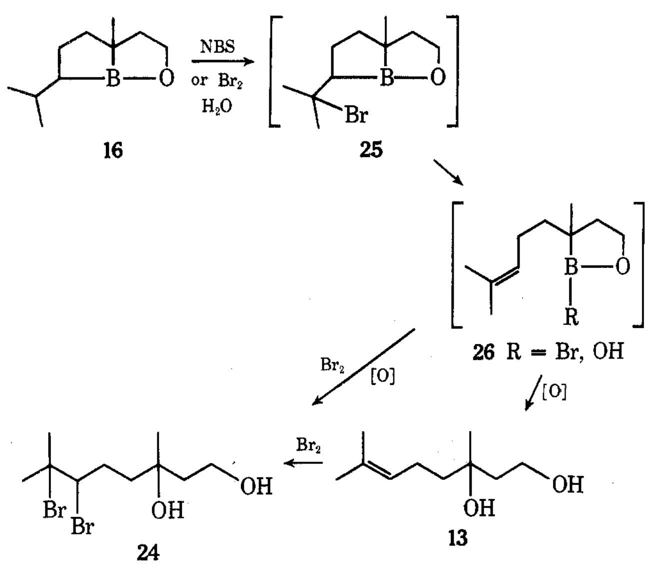
Hydroboration-oxidation of citral (**14**)[10] gave 3,7-dimethyl-1,2,6-octanetriol (**18**) containing 30% of the 1,3,6-triol **2**. Distillation of the alkylboranes formed from the hydroboration of citral (**14**) or geraniol (**15**)[11] with borane in THF afforded a 22% yield of 8-isopropyl-5-methyl-1-bora-2-oxabicyclo[3.3.0]octane (**16**), bp 78° (0.7 mm), which crystallized upon standing, mp 48–51°. Oxidation of **16** afforded 3,7-dimethyl-1,3,6-octanetriol (**2**) (Scheme II).

Oxidation of the nonvolatile organoboranes which remain after the distillation of borabicyclooctane **16** (pot temperatures of 185° were attained) gave 70% (46% yield) of 3,7-dimethyl-1-octen-6-ol (**20**) and 20% (13% yield) of 3,7-dimethyl-1,6-octanediol (**21**), along with ca. 10% of geraniol (**15**). The identity of **20** was confirmed by NMR analysis and by comparison of its ir spectrum with that published by Mitzner.[12] The structure of **21** was confirmed by oxidation to keto acid **22** using the Jones procedure and by comparison of spectral data with an authentic sample prepared via the hydroboration of citronellol (**23**). These products may be explained in terms of a thermal elimination reaction[6] (100–185°) of **17** to **19**. Monoalcohol **20** arises from oxidation of the elimination product **19**. Transfer of boron[13] from **17a** to **19** would afford boranes which upon oxidation would give diol **21** and geraniol (**15**).

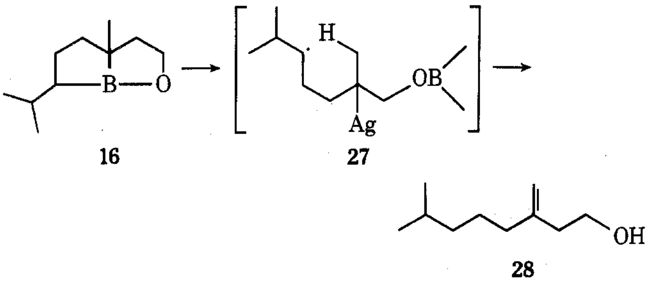
Several unsuccessful attempts were made to apply known methods for carbon-carbon bond formation to borane **16** in an effort to produce the cyclobutane carbon skeleton of grandisol.[14] Reaction of **16** with bromine or NBS in the presence of water[15] followed by oxidation afforded **24** and **13**, respectively. Bromination must take place preferentially at the tertiary carbon affording **25**, which is followed immediately by a β-elimination of the β-haloborane[4,16] to **26**, which in turn goes on to the observed products as shown in Scheme III.

An attempted free-radical coupling[17] of **16** by reaction with silver oxide using a variety of conditions also proved unsuccessful, as disproportionation product **28**[18] accounted for 40% of the material recovered, along with 40% of a mix-

Scheme III



ture of saturated and unsaturated diols and 20% of dimers. No trace of a cyclobutane derivative was found.



Experimental Section[19]

Hydroboration of Linalool (1) with Excess BH$_3$. To 5.0 g (32 mmol) of linalool (1) in 20 ml of dry THF at 0° under nitrogen was added dropwise 15 ml of 3 *M* BH$_3$ in THF (45 mmol). The solution was allowed to warm to room temperature overnight and was oxidized by the careful addition of 30 ml of 3 *N* NaOH and 20 ml of 30% H$_2$O$_2$ (176 mmol). After 3 hr, the layers were separated and the aqueous phase extracted with ether. The organic solution was washed with water and dried (MgSO$_4$) and the solvent was removed, leaving 4.55 g of viscous liquid (76%). A 3-g portion of the liquid was distilled, yielding two fractions. The first fraction, 0.4 g, bp 120° (0.1 mm), n^{20}D 1.4594, contained 3,7-dimethyl-2,6-octanediol (3) contaminated by approximately 20% of the 3,6-diol (4): ir 3.0 (OH), 6.75, 7.25, 9.5, 10.15, 10.7, and 11.25 μ; NMR (CDCl$_3$) 0.90 (d, 9, *J* = 7 Hz, CHCH$_3$), 1.13 (d, 3, J = 6 Hz, CHCH$_3$), 1.16 (s, HOCCH$_3$, compound 4), 1.3–1.9 (m, 6), 2.75 (m, 2, OH), 3.30 (m, 1, CHOH), 3.70 ppm (m, 1, HOCHCH$_3$).

The second fraction, 2.0 g, bp 135° (0.1 mm), contained 70% of 3,7-dimethyl-1,3,6-octanetriol (2) and 30% of diol 3 by NMR analysis. The residue, 0.5 g, was pure triol 2: n^{20}D 1.4689; ir 3.0, 8.8, 9.5, and 9.9 μ; NMR (CDCl$_3$) 0.91 [d, 6, *J* = 6 Hz, CH(CH$_3$)$_2$], 1.21 (s, 3, HOCCH$_3$), 1.3–2.0 (m, 7), 3.30 (m, 1, CHOH), 3.80 (t, 2, *J* = 6 Hz, CH$_2$OH), 4.5 ppm (m, 3, OH).

Oxidation of Diols 3 and 4 with Jones Reagent. A few drops of diols 3 and 4 were dissolved in 5 ml of acetone and titrated with Jones reagent at room temperature. Isopropyl alcohol and ether were added and the liquid was decanted, washed with water and sodium bicarbonate solution, and dried (MgSO$_4$). The solvents were removed, affording a nonviscous liquid consisting of two components which were separated by thin layer chromatography (50% ether–pentane). 3,7-Dimethyl-2,6-octanedione (5), 70% of the crude mixture as determined by NMR analysis, showed R_f 0.60; ir 5.80 (C=O), 6.85, 7.35, 8.05, and 8.6 μ; NMR (CDCl$_3$) 1.08 [d, 6, *J* = 7 Hz, CH(CH$_3$)$_2$], 1.10 (d, 3, CHCH$_3$), 1.80 (m, 2, CH$_2$), 2.12 (s, 3, COCH$_3$), 2.35–2.75 ppm (m, 4). 4-Methyl-4-hydroxyhexanoic acid lactone (6), 25% by NMR, displayed R_f 0.35; ir 5.65 (C=O), 6.85, 7.25, 8.08, 8.6, 8.85, 9.1, 9.45, and 10.70 μ; NMR (CDCl$_3$) 0.97 (t, 3, *J* = 7.5 Hz, CH$_2$CH$_3$), 1.37 (s, 3, CH$_3$), 1.71 (q, 2, *J* = 7.5 Hz, CH$_2$CH$_3$), 1.9–2.3 (m, 2, CH$_2$), 2.60 ppm (m, 2, CH$_2$CO); mass spectrum[20] *m/e* (rel intensity) 128 (1), 113 (14), 99 (82), 84 (9), 73 (18), 71 (15), 69 (22), 57 (18), 56 (22), 55 (25), 43 (100), 42 (10), 41 (25), 39 (17).

Preparation of 3,7-Dimethyl-1-octene-3,6-diol (8). To 10.0 g (65 mmol) of linalool (1) in 40 ml of dry THF was added dropwise at 0° 14.6 ml (43.8 mmol) of 3 *M* BH$_3$ in THF. After stirring overnight at room temperature, oxidation and work-up were effected in the usual manner. Distillation afforded 2.8 g (28%) of recovered linalool (1), bp 48–70° (0.2 mm), and 3.8 g (34% yield) of a viscous oil, bp 80° (0.1 mm), identified as 3,7-dimethyl-1-octene-3,6-diol (8): ir 3.0 (OH, intensity $\simeq$ to CH), 6.1 w (C=C); NMR (CDCl$_3$) 0.90 [d, 6, *J* = 6 Hz, CH(CH$_3$)$_2$], 1.27 (s, 3, HOCCH$_3$), 1.35–1.80 (m, 5), 3.32 (m, 3, OH and CHOH) or 3.28 (m, 1, CHOD with D$_2$O), 4.86–5.38 (m, 2, CH=CH$_2$), 5.65–6.20 ppm (m, 1, CH=CH$_2$). The residue, 0.9 g (9%), contained 3,7-dimethyl-1,3,6-octanetriol (2) by ir analysis.

The monoacetate 9, prepared by heating 700 mg of diol 8 with 1.2 ml of pyridine and 550 mg of acetic anhydride at 80° for 1 hr, showed n^{20}D 1.4490, and ir and NMR spectra consistent with those reported by Demole and Enggist.[3]

Preparation of 3,7-Dimethyl-6-octene-1,3-diol (13). To 16.9 ml (11.2 g, 160 mmol) of 2-methyl-2-butene in 50 ml of dry THF was added 26.6 ml of 3 *M* BH$_3$ in THF (80 mmol). The solution was stirred at ambient temperature for 2 hr, followed by the addition of 5.0 g (32 mmol) of linalool (1) at 0°. The reaction mixture was stirred for 0.5 hr at 0° and then for 2.5 hr at 25°. After oxidation and work-up, distillation afforded 1.8 g (36%) of unreacted linalool (1), bp 48° (0.1 mm), and 2.1 g (38%) of 3,7-dimethyl-6-octene-1,3-diol (13): bp 100° (0.1 mm); n^{20}D 1.4690 [lit.[21] bp 149–150° (10 mm), n^{20}D 1.4737]; ir 3.0 (OH), 6.9, 7.3, 9.0, and 9.5 μ; NMR (CDCl$_3$) 1.22 (s, 3, HOCCH$_3$), 1.35–2.3 (m, 6), 1.62 and 1.69 [s, 6, C=C(CH$_3$)$_2$], 3.5 and 3.9 (m, 2, OH, disappears with D$_2$O), 3.83 (t, 2, *J* = 6 Hz, CH$_2$OH), 5.13 ppm (m, 1, C=CH); mass spectrum *m/e* (rel intensity) 170 (2), 154 (19), 121 (37), 109 (41), 95 (25), 81 (35), 71 (39), 69 (93), 68 (20), 67 (30), 59 (20), 55 (42), 43 (100), 41 (88), 39 (31), 18 (29). The residue (0.2 g) appeared to be mainly 1,3,6-triol 2.

Hydroboration–Oxidation of Citral (14). To 5.0 g (33 mmol) of citral (14) in 30 ml of dry THF at 0° was added 11 ml of 3.0 *M* BH$_3$ in THF (33 mmol) and the reaction mixture was stirred under a nitrogen atmosphere. Aliquots withdrawn from the reaction mixture and hydrolyzed indicated that 7.6% of the hydride remained after 5 min, and only 0.9% after 3 hr. The boranes were oxidized by the usual procedure to give 5.3 g of viscous oil. Distillation afforded 0.5 g of geraniol–nerol (15), bp 65–95° (0.2 mm), an intermediate fraction, 1.0 g, bp 100–140° (0.2 mm), and 2.5 g (63% yield) of a very viscous colorless liquid, determined by NMR analysis to contain 30% of 3,7-dimethyl-1,3,6-octanetriol (2) and 70% of the corresponding 1,2,6-triol 18: bp 142° (0.1 mm); n^{20}D 1.4705; ir 2.98 μ (OH, stronger than CH); NMR (CDCl$_3$) 0.90 (d, 9, *J* = 6 Hz, CHCH$_3$), 1.22 (s, HOCCH$_3$, triol 2), 1.3–1.9 (m, 6), 3.2–4.0 ppm (m, 7).

Anal. Calcd for C$_{10}$H$_{22}$O$_3$: C, 63.12; H, 11.66. Found: C, 63.41; H, 11.60.

The presence of a 1,2-diol was confirmed by a positive periodate test.

Preparation of 8-Isopropyl-5-methyl-1-bora-2-oxabicyclo[3.3.0]octane (16). To 110 ml of 3.0 *M* BH$_3$ in THF (0.33 mol) and 200 ml of dry THF at 0° was added over 1 hr 50 g (0.325 mol) of geraniol (15, a 7:3 mixture of *E* and *Z* isomers) in 70 ml of THF. The solution was allowed to warm to room temperature over 2 hr followed by the addition of 3 ml of methanol to destroy excess hydride. Removal of solvent under reduced pressure and distillation afforded two fractions which distilled slowly at pot temperatures between 135 and 185°. The first fraction was borane 16, a very viscous, air-sensitive oil, 11.70 g (22% yield), bp 78° (0.7 mm), which formed white crystals upon standing, mp 48–51°: ir (CDCl$_3$) 3.42 (CH), 7.4 br, and 12.6 μ; NMR (CDCl$_3$) 0.90 (m, 9), 1.2–2.3 (m, 8), and 3.6–4.2 ppm (m, 2). A portion of the crystalline organoborane 16 was oxidized by the usual procedure yielding 3,7-dimethyl-1,3,6-octanetriol (2), n^{20}D 1.4670.

The second fraction, 3.72 g (7%), bp 120° (0.8 mm), was a nonviscous liquid which displayed ir (neat) 3.1, 3.4, 6.1 w, 6.85, 7.0–8.5, 10.01, and 11.05 μ; NMR (CDCl$_3$) 0.92 (m, 9), 1.1–2.3 (m, 8), 3.5–6.0 ppm (m, 2). A 1.0-g portion of the liquid was oxidized by the standard procedure, yielding 1.0 g of a material which was separated by preparative thin layer chromatography (60% ether–pentane) to afford 40% of 3,7-dimethyl-1-octen-6-ol (20), R_f 0.80: ir 3.0 (OH), 6.1, 10.05, and 11.0 μ (identical with the spectrum published by Mitzner[12]); NMR ($CDCl_3$) 0.91 [d, 6, J = 6 Hz, $CH(CH_3)_2$], 1.0 (d, 3, J = 6 Hz, $CHCH_3$), 1.3–2.2 (m, 6), 3.35 (m, 1, CHOH), 4.7–5.1 (m, 2, $CH{=}CH_2$), 5.4–6.0 ppm (m, 1, $CH{=}CH_2$), and ca. 50% of an unidentified material, R_f 0.27, which gave a negative periodate test and was tentatively identified as a diol on the basis of its R_f value: ir 3.0 (OH, weaker than CH) and 9.50 μ; NMR ($CDCl_3$) 0.89 (d, 3, J = 6 Hz), 0.90 (d, 3, J = 6.5 Hz), 1.1–1.9 (m, 10), 3.0–4.0 ppm (m, 4).

The nonvolatile alkylborane residue (**17**, 39 g) which had been heated to 185° during the distillation of **16** was dissolved in 150 ml of THF, oxidized with alkaline hydrogen peroxide, and worked up by the usual procedure. Distillation afforded 16.7 g (46% yield) of **20**, bp 70° (1.0 mm), $n^{20}D$ 1.4538, which was found to be contaminated by ca. 10% of geraniol (**15**) by GLC analysis using a 150-ft OS-138 column at 185°. A second fraction, 6.0 g (13% yield), bp 102–106° (0.1 mm), $n^{20}D$ 1.4638, was purified by thin layer chromatography (60% ether–pentane) to give pure 3,7-dimethyl-1,6-octanediol (**21**), R_f 0.29: ir 3.0 (OH, weaker than CH), 6.85, 7.25, and 9.50 μ (CH_2O); NMR ($CDCl_3$) 0.90 (d, 9, $CHCH_3$), 1.1–1.8 (m, 8), 3.28 (m, 1), 3.64 ppm (t, 3, J = 6 Hz, CH_2OH).

Anal. Calcd for $C_{10}H_{22}O_2$: C, 68.91; H, 12.73. Found: C, 68.16; H, 12.72.

A few drops of diol **21** were dissolved in 5 ml of acetone and titrated with Jones reagent. The usual work-up gave a pale yellow oil identified as 3,7-dimethyl-6-oxooctanoic acid (**22**): ir 2.8–4.0 and 5.85 μ; NMR ($CDCl_3$) 0.97 (d, 3, J = 6 Hz, $CHCH_3$), 1.08 [d, 6, J = 7 Hz, $CH(CH_3)_2$], 1.4–1.8 (m, 3), 2.0–2.8 ppm (m, 5).

Preparation of 3,7-Dimethyl-1,6-octanediol (21). To 5.0 g (32 mmol) of citronellol (**23**) in 20 ml of THF at 0° under nitrogen was added dropwise 10.7 ml of 3.0 M BH_3 (32 mmol). The solution was stirred at room temperature for 2 hr, cooled to 0°, and oxidized by the usual procedure. Work-up and distillation yielded 4.0 g (72% yield) of **21**, bp 105° (0.1 mm), $n^{20}D$ 1.4615, whose ir and NMR spectra were identical with those of the sample of **21** described above.

Reaction of 16 with Bromine. To a mixture of 1.76 g (10.6 mmol) of **16** in 20 ml of methylene chloride and 7.5 ml of H_2O at 0° under nitrogen was added 0.65 ml (1.90 g, 11.9 mmol) of bromine. The solution was allowed to warm to room temperature, and after 7 min the bromine color had dissipated. The mixture was again cooled to 0° and 16 ml of 3 N NaOH was added followed by 15 ml of ethanol and 3.5 ml of 30% H_2O_2 (32.6 mmol). The solution was stirred at 0° for 0.5 hr and then refluxed for 1.5 hr. The organic layer was separated, washed with saturated salt solution, and dried ($MgSO_4$) and the solvents removed, leaving 2.40 g of viscous yellow oil containing 75% of 3,7-dimethyl-6,7-dibromo-1,3-octanediol (**24**) by NMR and thin layer chromatographic analyses.

A pure sample of **24** was obtained by thin layer chromatography: ir 3.0 (OH), 3.4, 6.84, 7.30, 9.1, and 9.4 μ; NMR ($CDCl_3$) 1.29 (s, 3, $HOCCH_3$), 1.5–2.5 (m, 6), 1.83 and 2.00 [s, 6, $BrC(CH_3)_2$], 2.71 (s, 2, OH), 3.92 (t, 2, J = 6 Hz, CH_2OH), 4.1–4.3 ppm (m, 1, CHBr). The NMR and ir spectra were identical with those of an authentic sample of **24** prepared by the addition of bromine to **13**.

Anal. Calcd for $C_{10}H_{20}O_2Br_2$: C, 36.17; H, 6.07; Br, 48.12. Found: C, 35.85; H, 5.61; Br, 47.90.

Reaction of 16 with *N*-Bromosuccinimide. To 1.0 g (6.02 mmol) of borabicyclooctane **16** in 20 ml of CCl_4 under nitrogen was added 1.07 g (6.02 mmol) of NBS. The mixture was refluxed for 1 hr and cooled to 0°, and 10 ml of water was added. After stirring for 10 min, 6 ml of 3 N NaOH, 15 ml of ethanol, and 2.5 ml of 30% H_2O_2 were added, and the mixture was refluxed for 1 hr. The aqueous phase was extracted with CCl_4, the organic solution was washed (NaCl solution) and dried ($MgSO_4$), and the solvent was removed, leaving 0.8 g of yellow liquid. The products were separated by preparative thin layer chromatography (40% ether–pentane). The first band, R_f 0.88 (20%), appears to be a mixture of partially oxidized organoboranes as the compound burns with a bright green flame characteristic of boron. The second band, R_f ≤0.1, was reeluted using a 2:3:2 mixture of methanol, ether, and pentane to yield 50% of 3,7-dimethyl-6-octene-1,3-diol (**13**) containing a minor impurity which displayed an isopropyl doublet at 0.90 ppm. The NMR and ir spectra of **13** were identical with those of an authentic sample prepared by the hydroboration of linalool (**1**) with disiamylborane.

Reaction of Borabicyclooctane 16 with Silver Oxide. To an aqueous suspension of alkaline silver oxide (25 mmol) under nitrogen at 0° was added 1.8 g (10.8 mmol) of **16** in 12 ml of THF. The brown color of the silver oxide turned gray-black as silver formed. The mixture was stirred at ambient temperature for 2.5 hr, the silver was removed by filtration, and 5 ml of 30% hydrogen peroxide was added. The mixture was refluxed for 1 hr, cooled, and extracted with pentane. The organic solvents were removed, leaving 1.1 g of yellow oil which was distilled affording (a) 0.4 g, bp 56–60° (0.5 mm), $n^{20}D$ 1.4541; (b) 0.4 g, bp 96–100° (0.5 mm), $n^{20}D$ 1.4625; and (c) 0.2 g of residue. GLC of the low-boiling fraction on a OS-138 capillary column indicated that 80% of the fraction was comprised of one compound. A pure sample of 7-methyl-3-methylene-1-octanol (**28**) was obtained by GLC using a 12-ft DC-200 column at 200° (retention time 10 min) and showed ir 3.02, 6.08, 6.82, 7.25, 7.32, 9.55, and 11.25 μ; NMR ($CDCl_3$) 0.87 [d, 6, J = 6 Hz, $CH(CH_3)_2$], 1.1–2.1 (m, 8), 2.30 (t, 2, J = 6.5 Hz, $C{=}C{-}CH_2CO$), 3.68 (t, 2, J = 6.5 Hz, $-CH_2OH$), and 4.85 ppm (2, $-C{=}CH_2$). The mass spectrum showed a molecular ion at m/e 156.

The higher boiling fraction was a viscous oil which appeared to be a mixture of saturated and unsaturated diols as indicated by ir and NMR analysis.

Registry No.—**1**, 78-70-6; **2**, 57196-95-9; **3**, 31206-60-7; **4**, 57196-96-0; **5**, 57196-97-1; **6**, 2865-82-9; **8**, 57196-98-2; **13**, 27415-10-7; **14**, 5392-40-5; (*E*)-**15**, 106-24-1; (*Z*)-**15**, 106-25-2; **16**, 57196-99-3; **17**, 57197-00-9; **18**, 57197-01-0; **20**, 18479-56-6; **21**, 53067-10-0; **22**, 589-60-6; **23**, 106-22-9; **24**, 57197-02-1; **28**, 57197-03-2; 2-methyl-2-butene, 513-35-9; bromine, 7726-95-6; *N*-bromosuccinimide, 128-08-5.

References and Notes

(1) R. H. Cornforth, J. W. Cornforth, and G. Popják, *Tetrahedron*, **18**, 1351 (1962).

(2) Lactone **6** may be formed via dehydration and oxidation of a γ-lactol[3] formed from the anticipated hydroxy ketone.

(3) E. Demole and P. Enggist, *Helv. Chim. Acta*, **54**, 456 (1971).

(4) H. C. Brown and O. J. Cope, *J. Am. Chem. Soc.*, **86**, 1801 (1964).

(5) Brown has observed that the hydroboration of allyl alcohol occurs with 24% of the attack by boron at the 2 position.[4]

(6) H. C. Brown and R. M. Gallivan, *J. Am. Chem. Soc.*, **90**, 2906 (1968), and references cited therein.

(7) An intermolecular addition of B–H to **12** is not likely to take place at the tertiary carbon, since diborane is known to attack the tertiary position of 2-methyl-2-butene only to the extent of 2%.[8]

(8) H. C. Brown, "Boranes in Organic Chemistry", Cornell University Press, Ithaca, N.Y., 1972, p 265.

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

(10) Citral is a 2:1 mixture of the *E* and *Z* isomers geranial and neral.

(11) Geraniol and nerol are the *E* and *Z* isomers of 3,7-dimethyl-2,6-octen-1-ol, commonly referred to as geraniol. Varying the relative proportions of the isomers had little effect on the yield of **16**.

(12) B. M. Mitzner, V. J. Mancini, S. Lemberg, and E. T. Theimer, *Appl. Spectrosc.*, **22**, 34 (1968).

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(16) H. C. Brown and K. A. Keblys, *J. Am. Chem. Soc.*, **86**, 1791 (1964).

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(18) Compound **28** can be viewed as arising via an intramolecular hydrogen transfer in a radical such as **27**.

(19) All melting and boiling points are uncorrected. Refractive indices were determined on a Bausch and Lomb Abbe-3L refractometer and are uncorrected. NMR spectra were determined with Varian Associates A-60 and Perkin-Elmer R32 spectrometers. Infrared spectra were recorded on a Perkin-Elmer Infracord spectrometer. Mass spectra were recorded at 70 eV on a Hitachi RMU-6A mass spectrometer. Thin layer chromatography was carried out using 20 × 20 cm plates (Brinkman silica gel PF-254, 1 mm thickness). Microanalyses were performed by Dr. C. S. Yeh and associates.

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