stirred reaction mixture. The reaction started immediately. The temperature of the reaction mixture was kept between −20 and 30°. After the addition of the boron halide, the reaction mixture was processed as in A.

All the haloalkylated products were known from the literature and were identified by their physical data, infrared and n.m.r. spectra, halogen analyses, and gas–liquid chromatography, using a Perkin-Elmer Model 154-C vapor fractometer.

The Hydroboration of Trialkylated Ethylenes. The Configurations of Carvomenthol and Its Geometric Isomers

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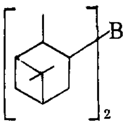
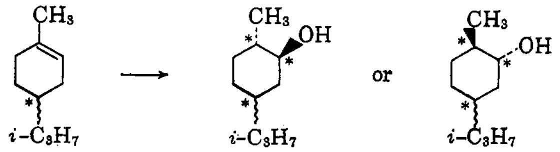
While *cis* dialkylated ethylenes undergo asymmetric, stereoselective hydroboration with optically active diisopinocampheylborane, trialkylated ethylenes undergo hydroboration stereoselectively but not asymmetrically. The results of the hydroboration of 1-*p*-menthene provide a direct chemical basis on which to make configurational assignments for the 2-*p*-menthanol geometric isomers.

A few years ago Brown and Zweifel[1] reported the conversion of *cis* dialkylated ethylenes to the corresponding optically active secondary alcohols *via* hydroboration, oxidation, and hydrolysis. The key step in the sequence involved the use of optically active diisopinocampheylborane (I) to achieve asymmetric, stereoselective hydroboration.



I

This paper reports the results of our attempts to prepare optically pure secondary alcohols from trialkylated ethylenes *via* the same reaction sequence. The objective was to prepare any one of the 2-*p*-menthanol optical isomers free of its enantiomer and diastereoisomers. Hydroboration of the readily available (+)-1-*p*-menthene[2] with I seemed to offer an efficient, direct route free of troublesome isomer separation problems. The over-all reaction (hydroboration, oxidation, and hydrolysis) was visualized as taking place as shown.



II III IV

Thus, (+)-1-*p*-menthene would provide the optical purity required in position 4 of the product, and efficient, asymmetric, stereoselective hydroboration would provide the optical purity required at positions 1 and 2 of the product.

Before experimenting with diisopinocampheylborane (I) of high optical purity, a more readily obtainable material, containing about 75% of one optical isomer and about 25% of the other, was used. The anticipated end product would be a mixture of diastereoisomers III and IV in the same ratio as that of the enantiomers in the hydroborating agent, *i.e.*, 3 to 1, or 1 to 3. Such a result would justify the hydroboration of II with less plentiful diisopinocampheylborane (I) of high optical purity to obtain a single 2-*p*-menthanol optical isomer. After the steps of hydroboration, oxidation, and hydrolysis, (−)-carvomenthol, $[\alpha]^{25}\text{D}$ −25.40°, and (+)-isocarvomenthol, $[\alpha]^{25}\text{D}$ +16.30°, were isolated in a *1.3 to 1.0 ratio.* Based on these specific rotations, both compounds are at least 90% optically pure.[3]

Hydroboration of the same olefin with diborane also gave carvomenthol and isocarvomenthol in the same ratio. Thus, the optical activity of the diisopinocampheylborane (I) played no special role in controlling the optical purity of positions 1 and 2 of the product, and asymmetric hydroboration did not take place.

In order to determine the structural features of 1-*p*-menthene which preclude asymmetric, stereoselective hydroboration, the hydroboration of two simple olefins, *cis*-2-butene and 3-methyl-2-butene, with the hydroborating agent I of high optical purity was studied. *cis*-2-Butene, the simplest *cis* dialkylated ethylene, has been converted with this hydroborating agent by Brown and Zweifel[1] to 2-butanol of 87% optical purity. In our hands, *cis*-2-butene yielded 2-butanol, $[\alpha]^{25}\text{D}$ −12.0°. Leroux and Lucas[4] report $[\alpha]^{25}\text{D}$ −13.51° for L(−)-2-butanol. Hence our product is about 89% optically pure and the experiment confirms the work of Brown and Zweifel.[1] On the other hand, 3-methyl-2-butene, the simplest trialkylated ethylene, yielded 3-methyl-2-butanol, $[\alpha]^{25}\text{D}$ +0.4°. Pickard and Kenyon[5] report $[\alpha]^{20}\text{D}$ +4.85° for (+)-3-methyl-2-butanol. Hence our product is only about 8% optically pure.

These experiments show that, while *cis* dialkylated ethylenes undergo asymmetric, stereoselective hydroboration with I, trialkylated ethylenes do not. Thus, branching on one carbon atom of an olefinic bond precludes asymmetric addition of optically active diisopinocampheylborane. It should be remembered that α-pinene (a trialkylated ethylene) reacts asymmetrically with diborane but does not react with diisopinocampheylborane.[1]

Zweifel, *et al.*,[6] have pointed out the importance of the asymmetric bulk of optically active diisopinocampheylborane in the asymmetric, stereoselective hydro-

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(1) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 486 (1961).

(2) W. F. Newhall, *J. Org. Chem.*, **23**, 1274 (1958).

(3) J. L. Simonsen ["The Terpenes," Vol. 1, Cambridge University Press, Cambridge, 1947, p. 252] lists the following specific rotations at 16° for 2-*p*-menthanol isomers: *d*-carvomenthol, +26°; *l*-isocarvomenthol, −18°; *l*-neocarvomenthol, −42°; *l*-neoisocarvomenthol, −35°.

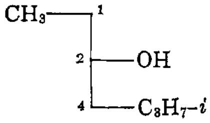
(4) P. J. Leroux and H. J. Lucas, *J. Am. Chem. Soc.*, **73**, 41 (1951).

(5) R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **101**, 620 (1912).

(6) G. Zweifel, N. R. Ayyangar, and H. C. Brown, *J. Am. Chem. Soc.*, **84**, 4342 (1962).

boration of *cis* dialkylated ethylenes. Brown and Zweifel[1] have shown that trialkylboranes are produced in these reactions. Our experiments indicate that trialkylated ethylenes do not form trialkylboranes efficiently by reaction with I. A partial detachment from boron of the optically active alkyl groups originally attached to boron in the hydroborating agent has been observed instead. In hydroboration reactions in which the molar ratio of 1-*p*-menthene to diisopinocampheylborane was varied from 0.5 to 1.0, α-pinene was observed as a product. Moreover, the amount of α-pinene formed was directly proportional to the menthene–diisopinocampheylborane molar ratio. This increase in α-pinene concentration with increasing 1-*p*-menthene concentration suggests a displacement reaction in which 1-*p*-menthene effects a displacement of isopinocampheyl groups from boron. Zweifel, *et al.*,[7] attribute the formation of α-pinene in the reaction of the *trans* dialkylated ethylene, *trans*-4-methyl-2-pentene, with diisopinocampheylborane to a disproportionation of the hydroborating agent prior to the hydroboration of the slowly reacting *trans* olefin. Whatever the actual reaction path of trialkylated ethylenes with bulky hydroborating agents may prove to be, it is different from that of *cis* dialkylated ethylenes.[6]

This work has made possible the assignments of geometric configuration for the 2-*p*-menthanol isomers. The four geometric configurations are shown schematically.



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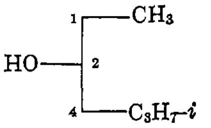
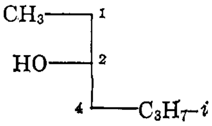
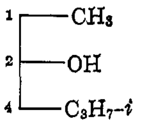


VI



VII



VIII

Read, *et al.*,[8] have shown that carvomenthol and neocarvomenthol are epimeric at position 2. They have offered strong indirect evidence that the methyl and isopropyl groups in these two isomers are in the *trans* configuration, and have assigned structure V to carvomenthol and structure VII to neocarvomenthol. Bose,[9] on the basis of conformational analysis, agrees with these assignments. Bose[9] seems to have made the only structural assignments to the remaining two isomers, having suggested that isocarvomenthol is VIII, and that neoisocarvomenthol is VI. These latter two assignments are the reverse of the assignments which shall be made in this paper on the basis of direct chemical evidence.

The work presented proves that both carvomenthol and isocarvomenthol contain methyl and hydroxyl groups in the *trans* configuration because in the preparation of these isomers *via* the hydroboration of 1-*p*-menthene, the hydrogen atoms at positions 1 and the hydroxyl groups at positions 2 are affixed in the *cis* configuration.[10] If, as argued by Read and others,[8] carvomenthol has methyl and isopropyl groups in the *trans* configuration, carvomenthol is indeed V and isocarvomenthol must be VI; and since carvomenthol and neocarvomenthol are epimeric at position 2, neocarvomenthol must be VII and neoisocarvomenthol, VIII.

Experimental

Materials.—A sample of (+)-α-pinene, $[\alpha]^{25}\mathrm{D}$ +47.8°, was kindly furnished by Dr. Frances Greer of the Research Department, Naval Stores Division, Hercules Powder Co.

Hydroboration Reaction.—In the preparation of hydroborating agents and in the hydroboration reactions, established procedures were followed.[1,11]

Gas Chromatographic Analysis of Products.—Reaction mixtures were analyzed on a Perkin-Elmer Model 154C instrument with a thermistor-type detector and a 12 ft. × 0.25 in. o.d. stainless steel column packed with 25% poly-1,2-butanediol succinate on acid-washed Chromosorb W. Column temperature was 150° and helium flow rate was 65 ml./min.

Isolation of Reaction Products.—The butanols and the menthanols were isolated by gas chromatography using a Wilkens Autoprep Model A-700 instrument operated isothermally. For the butanols, a 20 ft. × 0.375 in. o.d. aluminum column packed with 25% Carbowax 20M on acid-washed silanized Chromosorb W was used. Repetitive automatic 50-μl. samples were chromatographed at 150° column temperature and 200 ml./min. helium flow rate. For the menthanols, a 55 ft. × 0.375 in. o.d. aluminum column packed with 25% poly(diethylene glycol) succinate on acid-washed, silanized Chromosorb W was used. Automatic repetitive on-column 200-μl. injections were made at 160° column temperature, 310° detector temperature, and 200 ml./min. helium flow rate.

Menthanol Derivatives.—3,5-Dinitrobenzoates were prepared in the usual manner and recrystallized from absolute ethanol. The derivative of (−)-carvomenthol had m.p. 104–104.5°; that of (+)-isocarvomenthol, m.p. 108.5–109°. Melting points were determined in capillary tubes and are uncorrected. Simonsen[3] lists m.p. 107, 111, 129, and 71–72°, respectively, for the 3,5-dinitrobenzoates of *d*-carvomenthol, *l*-isocarvomenthol, *l*-neocarvomenthol, and *l*-neoisocarvomenthol.

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[7] G. Zweifel, N. R. Ayyangar, and H. C. Brown, *J. Am. Chem. Soc.*, **85**, 2072 (1963).

[8] (a) J. Read and R. G. Johnston, *J. Chem. Soc.*, 226 (1934); (b) R. G. Johnston and J. Read, *ibid.*, 1138 (1935); (c) N. L. McNiven and J. Read, *ibid.*, 159 (1952).

[9] A. K. Bose, *Experientia*, **8**, 458 (1952).

[10] H. C. Brown and G. Zweifel [*J. Am. Chem. Soc.*, **81**, 247 (1959)] have shown conclusively that hydroboration of 1-methylcycloalkenes with diborane leads to *trans*-2-methylcycloalkanols.

[11] H. C. Brown and B. C. Subba Rao, *ibid.*, **81**, 6428 (1959).