

heated under reflux for 2 hr. The reaction mixture was cooled to room temperature and sufficient 3 *N* sodium hydroxide added to ensure an excess. The upper phase was separated and washed with cold water to remove diglyme. There was obtained 12.4 g. of crude *cis*-pinane. Analysis of the crude product by gas chromatography (squalene column) indicated 98% *cis*-pinane, 2% *trans*-pinane. The crude product was purified by gas chromatography. The *cis*-pinane collected exhibited  $n_D^{20}$  1.4624,  $\alpha_D^{20}$   $-19.3^\circ$  (1 dm.).

**Preparation of (-)-*trans*-Pinane from (-)- $\beta$ -Pinene.**<sup>34</sup>—Under identical conditions described above, 13.6 g. of (-)- $\beta$ -pinene was converted into the organoborane. The reaction mixture was then heated at 125° for 2.5 hr. to isomerize the product. The reaction mixture was cooled to room temperature, 11 ml. of propionic acid added, and the mixture heated for 2 hr. under reflux. The hydrocarbon product was isolated as for *cis*-pinane above. There was obtained 13.0 g. of crude product. Gas chromatographic examination indicated 98% *trans*- and 2% *cis*-pinane. The crude product was purified by gas chromatography on an acrylonitrile-glycerol column. The *trans*-pinane collected exhibited  $n_D^{20}$  1.4610,  $\alpha_D^{20}$   $-14.5^\circ$  (1 dm.).

**Preparation of *cis*-Pinane from (+)- $\alpha$ -Pinene.**<sup>34</sup>—In a 200-ml. flask was placed 13.6 g. of (+)- $\alpha$ -pinene (0.10 mole,  $[\alpha]_D^{20}$   $+47.6^\circ$ ) and 45 ml. of a 1.00 *M* solution of sodium borohydride in diglyme. Diborane was generated by adding to the reaction mixture 16.4 ml. of a 3.65 *M* solution of boron trifluoride in diglyme. The reaction flask was immersed in a water bath. The reaction was allowed to proceed for an additional 2 hr. at 20–25°. The excess hydride was destroyed by adding glycerol. The reaction mixture was treated with 11 ml. of propionic acid, then heated for 4 hr. under reflux. After cooling to room temperature, the reaction mixture was diluted with sufficient 3 *N* sodium hydroxide to ensure an excess of base. The upper layer was separated and washed with cold water to remove diglyme. Analysis of the crude product by gas chromatography (squalene column) indicated essentially pure *cis*-pinane. Preparative gas chromatography yielded 4.8 g., 35% yield, (+)-*cis*-pinane,  $n_D^{20}$  1.4614,  $\alpha_D^{20}$   $+21.5^\circ$  (1 dm.).

**Preparation of (-)-*cis*-Myrtaol from (-)- $\beta$ -Pinene.**<sup>34</sup>— $\beta$ -Pinene was hydroborated and oxidized in the usual manner. The reaction product, *cis*-myrtaol, was purified by gas chromatography using a tris-(cyanoethoxy)-propane column to remove a very minor amount of the *trans* isomer. The purified product exhibited the constants  $n_D^{20}$  1.4910,  $[\alpha]_D^{20}$   $-20.9^\circ$  (*c* 4, chloroform).

**Preparation of (-)-Isopinocampheol.**—In a 300-ml. flask, fitted with a dropping funnel, a reflux condenser, a nitrogen inlet tube, and a magnetically operated stirring bar, was placed 82.5

ml. of a 1.00 *M* solution of sodium borohydride in diglyme (10% excess), 27.2 g. of  $\alpha$ -pinene (0.20 mole,  $n_D^{20}$  1.4648,  $[\alpha]_D^{20}$   $+47.6^\circ$ ) in 20 ml. of diglyme. The flask was immersed in a water bath and flushed with nitrogen. A static nitrogen atmosphere was then maintained. From the dropping funnel 14 ml. of boron trifluoride etherate (0.11 mole) was added dropwise to the stirred reaction mixture over a period of 30 min., keeping the temperature at 20 to 25°. The flask was permitted to remain for 1 hr. at this temperature. The excess of hydride was destroyed by the careful addition of 20 ml. of water. The organoboronic acid thus formed ( $R_2BOH$ ) was oxidized at 30 to 50° by adding 22 ml. of 3 *N* sodium hydroxide, followed by the dropwise addition of 22 ml. of 30% hydrogen peroxide (vigorous reaction!). The flask was permitted to remain an additional hour at room temperature.

The reaction mixture was taken up with 150 ml. of ether, and the ether extract was washed five times with equal amounts of ice water to remove diglyme. The ether extract was dried over anhydrous magnesium sulfate. The product obtained after removal of the ether was crystallized from a small amount of petroleum ether (35–37°). There was obtained 24.3 g., 79% yield, of isopinocampheol, m.p. 55–57°,  $[\alpha]_D^{20}$   $-32.8^\circ$  (*c* 10, benzene), m.p. acid phthalate 125–126°, m.p. 3,5-dinitrobenzoate 98–99°.

**Preparation of Neoisopinocampheol.**—Isopinocampheol was oxidized by the procedure of Brown and Garg<sup>35</sup> to yield isopinocampheol, b.p. 54–56° at 1 mm.,  $n_D^{20}$  1.4745,  $\alpha_D^{20}$   $+10.3^\circ$  (1 dm.).<sup>36</sup>

Isopinocampheol (4.0 g., 26.3 mmoles) was added to 100 ml. of tetrahydrofuran containing 58 mmoles of lithium trimethoxyaluminumhydride.<sup>26</sup> The product was purified by gas chromatography on a Carbowax 20M column. The neoisopinocampheol isolated, 2.1 g., exhibited m.p. 45–47°,  $[\alpha]_D^{20}$   $+36^\circ$  (*c* 3, benzene); m.p. 3,5-dinitrobenzoate 102–103°.<sup>37</sup>

A sample of (+)-isopinocampheol, 6.0 g., was added to a solution of 1.25 g. of sodium in 40 ml. of ethanol. After 24 hr. at 25°, the product was isolated by steam distillation. Gas chromatographic examination revealed 81% pinocampheol and 19% isopinocampheol.

**Acknowledgment.**—We are greatly indebted to Dr. R. A. Bankert of the Hercules Powder Co., Wilmington, Del., for a generous gift of (+)- $\alpha$ -pinene, and to the Glidden Co., Jacksonville, Fla., for a gift of (-)- $\beta$ -pinene.

(35) H. C. Brown and C. P. Garg, *J. Am. Chem. Soc.*, **83**, 2952 (1961).

(36) Schmidt (ref. 4) reports  $n_D^{20}$  1.4748,  $\alpha_D^{20}$   $+10.5^\circ$  for isopinocampheol.

(37) Schmidt (ref. 4) reports m.p. 48°,  $[\alpha]_D^{20}$   $+36^\circ$  for neoisopinocampheol.

[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY, LAFAYETTE, IND.]

## Hydroboration. XVIII. The Reaction of Diisopinocampheylborane with Representative *cis*-Acyclic, Cyclic, and Bicyclic Olefins. A Convenient Synthesis of Optically Active Alcohols and Olefins of High Optical Purity and Established Configuration

By HERBERT C. BROWN, NAGARAJ R. AYYANGAR,<sup>1</sup> AND GEORGE ZWEIFEL

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Optically active diisopinocampheylborane, readily synthesized by the hydroboration of optically active  $\alpha$ -pinene, reacts readily with *cis*-2-butene to yield diisopinocampheyl-2-butylborane. Oxidation with alkaline hydrogen peroxide yields isopinocampheol and 2-butanol, the latter in optical purity of 87%. (+)- $\alpha$ -Pinene yields (-)-2-butanol ( $[\alpha]_D$   $-11.8^\circ$ ); (-)- $\alpha$ -pinene yields (+)-2-butanol ( $[\alpha]_D$   $+11.7^\circ$ ). The reaction appears to be general for a number of *cis*-acyclic, cyclic, and bicyclic olefins, and it has been applied to *cis*-2-butene, *cis*-2-pentene, *cis*-3-hexene, *cis*-4-methyl-2-pentene, and norbornene. The alcohols realized exhibit optical purities in the range of 65 to 91%. Treatment of an excess of an olefin racemate with the reagent results in the preferential reaction of one of the components. In this way, racemic mixtures of 3-methylcyclopentene, 3-ethylcyclopentene, and 1-methylnorbornene have been converted into optically active olefin products. The absolute configuration of diisopinocampheylborane may be deduced from the known configuration of  $\alpha$ -pinene. On the basis of a simple model for the hydroboration step it is possible to predict the absolute configuration of the optically active alcohols and olefins obtained in this asymmetric synthesis.

Dialkylboranes, readily accessible *via* hydroboration of hindered olefins, exhibit an unusually high selectivity for olefins with different structural features.<sup>2</sup> In view of these properties, it appeared possible that dialkylboranes derived from optically active terpenes or steroids might convert olefins into organoborane moieties capable of being transformed into optically active

derivatives. Preliminary experiments indicated that diisopinocampheylborane, derived from the hydroboration of optically active  $\alpha$ -pinene, is a highly selective hydroborating agent<sup>2</sup> and exhibits a remarkable asymmetric stereoselectivity when applied to the hydroboration of *cis*-olefins<sup>3</sup> and for the reduction of ketones.<sup>4</sup>

The subject matter of the present paper deals with a detailed study of the applicability of optically active

(1) Postdoctorate research associate on a grant provided by the National Science Foundation (G19878).

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

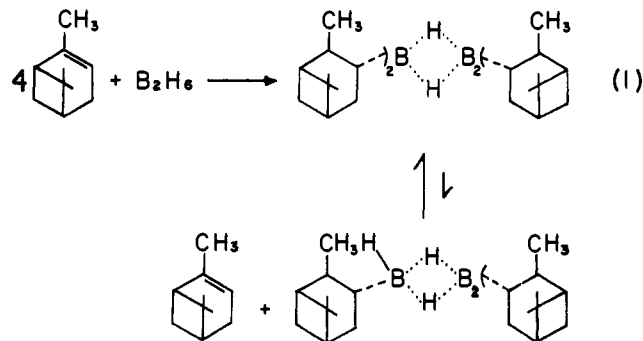
(3) A preliminary communication reporting this discovery was published earlier: H. C. Brown and G. Zweifel, *ibid.*, **83**, 486 (1961).

(4) H. C. Brown and D. B. Bigley, *ibid.*, **83**, 3166 (1961).

diisopinocampheylborane as a reagent for the asymmetric synthesis of optically active alcohols from olefins and for the resolution of olefin racemates.<sup>6</sup> Moreover, it will be shown that the configurations of the optically active alcohols obtained in this way can be successfully deduced by considering the absolute configuration of the reagent and the probable steric course of the reaction.<sup>6</sup>

### Results

**Diisopinocampheylborane.**— $\alpha$ -Pinene readily undergoes hydroboration at 0° to form *sym*-tetraisopinocampheylidiborane<sup>7,8</sup> (1). Even in the presence of



excess  $\alpha$ -pinene the reaction does not proceed further. Indeed, in the absence of excess  $\alpha$ -pinene, there is evidence for a significant dissociation of the tetraalkyl derivative into  $\alpha$ -pinene and triisopinocampheylidiborane<sup>9</sup> (1). The product is less soluble in diglyme than it is in tetrahydrofuran, and the amount of dissociated material is less in the former medium. Consequently, we have found it desirable to prepare and utilize the reagent in diglyme for reactions where it is evidently desirable to minimize the amount of dissociated product present.

Oxidation of the reaction product with alkaline hydrogen peroxide yields essentially pure isopinocampheol. The hydroboration reaction must, therefore, involve a pure *cis* addition of the boron-hydrogen group to the double bond—from the less hindered side of the molecule—the direction opposite to the *gem*-dimethyl group, followed by oxidation with retention of configuration.<sup>10</sup>

In the present study both dextrorotatory ( $[\alpha]_D +47.6^\circ$ ) and levorotatory ( $[\alpha]_D -47.9^\circ$ )  $\alpha$ -pinene were utilized, indicating optical purities in the 93 to 95% range.<sup>11</sup> Hydroboration of (+)- $\alpha$ -pinene affords (–)-*sym*-tetraisopinocampheylidiborane ( $[\alpha]_D -37.1^\circ$ ).<sup>8</sup> The following discussion is referred to (–)- and (+)-*sym*-tetraisopinocampheylidiborane, implying that the reagent was prepared from (+)- and (–)- $\alpha$ -pinene, respectively.

Finally, although this substance evidently exists in the solid state and in ether solvents as the dimeric diborane derivative, it has proved convenient to refer to it by its more simple monomeric name, diisopinocampheylborane,  $\text{IPC}_2\text{BH}$ , in applications and discussions where the dimeric structure does not appear to be a significant factor. This practice is purely one of convenience and should not be taken to imply that the reaction necessarily involves the monomeric species as an intermediate.

(5) H. C. Brown, N. R. Ayyangar, and G. Zweifel, *J. Am. Chem. Soc.*, **84**, 4341 (1962).

(6) G. Zweifel, N. R. Ayyangar, and H. C. Brown, *ibid.*, **84**, 4342 (1962).

(7) H. C. Brown and G. Zweifel, *ibid.*, **83**, 2544 (1961).

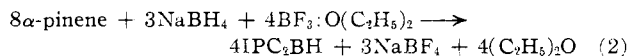
(8) H. C. Brown and G. J. Klender, *Inorg. Chem.*, **1**, 204 (1962).

(9) H. C. Brown and A. W. Moerikofer, *J. Am. Chem. Soc.*, **84**, 1478 (1962).

(10) G. Zweifel and H. C. Brown, *ibid.*, **86**, 393 (1964).

(11) F. H. Thurber and R. C. Thielke, *ibid.*, **53**, 1030 (1931), report  $[\alpha]_D +1.1^\circ$  for (+)- $\alpha$ -pinene.

The reagent, diisopinocampheylborane, was normally prepared by the following procedure. The calculated quantity of  $\alpha$ -pinene and sodium borohydride in diglyme, maintained at 0°, was treated with the theoretical quantity of boron trifluoride etherate over a period of 15 min. (2).



The product precipitates as a thick, white solid as the reaction proceeds. The mixture was maintained for an additional 4 hr. at 0°, prior to use, to ensure completion of the hydroboration reaction. The reagent appears to be quite stable under these conditions. In one case the product, after 48 hr. at 0°, was hydrolyzed and oxidized with alkaline hydrogen peroxide. There was obtained essentially pure isopinocampheol.

**Synthesis of Optically Active Alcohols.**—The reaction of (–)-diisopinocampheylborane with *cis*-2-butene at 0° proceeded rapidly and was complete in 2 to 4 hr. The progress of the reaction is apparent from the disappearance of the precipitate of the reagent. Oxidation of the organoborane with alkaline hydrogen peroxide gave (–)-2-butanol in 90% yield. Purification of the alcohol by gas chromatography afforded pure 2-butanol,  $[\alpha]_D -11.8^\circ$ , indicating an optical purity of 87%.<sup>12</sup> Hydroboration of *cis*-2-butene with (+)-diisopinocampheylborane, followed by oxidation, gave (+)-2-butanol,  $[\alpha]_D +11.7^\circ$ , an optical purity of 86%.

It is noteworthy that the trialkylborane is capable of maintaining asymmetry without significant racemization over long periods. Thus, a reaction mixture of *cis*-2-butene and (+)-diisopinocampheylborane, maintained at 25° for 48 hr. prior to oxidation, yielded (+)-2-butanol,  $[\alpha]_D +9.6^\circ$ , an indicated optical purity of 70%.

The hydroboration of *cis*-2-butene with the reagent in tetrahydrofuran produces 2-butanol of slightly lower optical purity than that realized in diglyme. Thus, 2-butanol, obtained from a reaction in which (+)-diisopinocampheylborane was synthesized and utilized in tetrahydrofuran solution, exhibited 78% optical purity instead of the 86% realized in diglyme.

The hydroboration of *cis*-3-hexene with (–)-diisopinocampheylborane proceeded at a rate similar to that realized with *cis*-2-butene. Oxidation gave (–)-3-hexanol,  $[\alpha]_D -6.5^\circ$ , indicating 91% optical purity.<sup>13</sup>

Hydroboration of *cis*-2-pentene with (+)-diisopinocampheylborane in diglyme, followed by oxidation, afforded a mixture of 2-pentanol (70%) and 3-pentanol (30%). Purification by gas chromatography yielded a product with a 76:24 distribution of 2- and 3-pentanol,  $[\alpha]_D +8.6^\circ$ . Since 3-pentanol is inactive, the observed rotation corresponds to an 82% optical purity for the (+)-2-pentanol.<sup>14</sup> An even higher selectivity of the boron atom of the reagent for the less hindered position of the double bond is observed in the hydroboration of *cis*-4-methyl-2-pentene with (+)-diisopinocampheylborane. Oxidation of the product gave a mixture of 4-methyl-2-pentanol (92%) and 2-methyl-3-pentanol (8%). Purification of the mixture by gas chromatography yielded (+)-4-methyl-2-pentanol,  $[\alpha]_D +16.0^\circ$ , indicating an optical purity of 76%.<sup>15</sup>

(12) P. J. Leroux and H. J. Lucas, *ibid.*, **73**, 41 (1951), report  $[\alpha]_D -13.5^\circ$  for (–)-2-butanol.

(13) J. Kenyon and R. Poplett, *J. Chem. Soc.*, 273 (1945), report  $[\alpha]_D -7.13^\circ$  for 3-hexanol.

(14) D. H. Brauns, *J. Research Natl. Bur. Standards*, **31**, 83 (1943), reports  $[\alpha]_D +13.9^\circ$  for 2-pentanol.

(15) J. Kenyon and H. E. Strauss, *J. Chem. Soc.*, 2153 (1949), report  $[\alpha]_D +21.2^\circ$  for 4-methyl-2-pentanol.

TABLE I

PREPARATION OF OPTICALLY ACTIVE ALCOHOLS *via* HYDROBORATION WITH DIISOPINOCAMPHEYLBORANE IN DIGLYME AT 0°

$\alpha$ -Pinene used	Olefin	Alcohol	Rotation, $[\alpha]_D^{20}$ , deg.	Optical purity, %
+	<i>cis</i> -2-Butene	2-Butanol	-11.8	87
-	<i>cis</i> -2-Butene	2-Butanol	+11.7	86
-	<i>cis</i> -2-Butene <sup>a</sup>	2-Butanol	+10.5	78
-	<i>cis</i> -2-Pentene	2-Pentanol, 76% 3-Pentanol, 24%	+ 8.6 <sup>b</sup>	82 <sup>c</sup>
+	<i>cis</i> -3-Hexene	3-Hexanol	- 6.5	91
-	<i>cis</i> -4-Methyl-2-pentene	4-Methyl-2-pentanol, 96% 2-Methyl-3-pentanol, 4%	+16.0 <sup>d</sup>	76 <sup>e</sup>
+	Norbornene	<i>exo</i> -Norborneol	- 2.0	67-70
-	Norbornene	<i>exo</i> -Norborneol	+ 1.95	65-68
+	Bicycloheptadiene <sup>f</sup>	<i>exo</i> -Dehydronorborneol	+ 5.8	48-51

<sup>a</sup> The reaction was carried out in tetrahydrofuran. <sup>b</sup> For the mixture of 2- and 3-pentanol. <sup>c</sup> Calculated for pure 2-pentanol. <sup>d</sup> For the mixture of 4-methyl-2-pentanol and 2-methyl-3-pentanol. <sup>e</sup> Calculated for pure 4-methyl-2-pentanol. <sup>f</sup> Ref. 17.

The hydroboration of norbornene with diborane occurs from the *exo* direction.<sup>7</sup> Similarly, the hydroboration of this olefin with (-)-diisopinocampheylborane, followed by oxidation, gave (-)-*exo*-norborneol,  $[\alpha]_D -2.0^\circ$  (*c* 3, chloroform), indicating an optical purity of 67-70%.<sup>16</sup> (+)-Diisopinocampheylborane yielded (+)-*exo*-norborneol,  $[\alpha]_D +1.95^\circ$ .

The reagent was recently utilized to achieve the conversion of bicycloheptadiene into *exo*-dehydronorborneol,  $[\alpha]_D +5.8^\circ$ , an indicated optical purity of 48 to 51%.<sup>17</sup>

These results are summarized in Table I.

The reaction of diisopinocampheylborane with several representative *trans*-olefins was also investigated. In the case of these olefins the reaction was much slower and did not involve a simple addition, since the hydroboration of the *trans*-olefin was accompanied by the liberation of  $\alpha$ -pinene. The alcohols obtained in the usual oxidation exhibited optical activity, but the optical purities proved to be much lower than those realized with the *cis*-olefins. Nevertheless, the results are of considerable interest, since it proved possible to achieve an empirical correlation of the absolute configurations of the products.<sup>18</sup>

**Preparation of Optically Active Olefins from Racemic Mixtures.**—The successful application of diisopinocampheylborane as an asymmetric hydroborating agent for *cis*-olefins suggested that it might serve for the selective hydroboration of one member of a pair of enantiomeric olefins. In this way the hydroboration of an olefin racemate with a deficient quantity of the reagent would convert the more reactive enantiomer into the organoborane, leaving the less reactive enantiomer free to be recovered in optically active form.

3-Methylcyclopentene was synthesized from 1-methylcyclopentene *via* the hydroboration reaction, as previously described.<sup>7</sup> Treatment of the racemic mixture of 3-methylcyclopentene with diisopinocampheylborane, in the mole ratio of two olefins per mole of the borane, yielded residual 3-methylcyclopentene,  $[\alpha]_D -34.6^\circ$ , indicating an optical purity of 45%.<sup>19</sup> Hydroboration of 3-methylcyclopentene with a larger relative quantity of the reagent yielded the olefin in a higher optical activity,  $[\alpha]_D -50.8^\circ$ , indicating an optical purity of 65%.

It is relatively simple to produce a mixture of 3- and 4-methylcyclopentene, but it is exceedingly difficult to isolate the pure olefins from such a mixture. Accordingly, a mixture of 3- (37%) and 4-methylcyclo-

pentene (63%) was treated with the reagent in the mole ratio of 2 to 1. Unfortunately, no change in the isomer ratio was achieved. However, the recovered olefin exhibited a rotation of  $[\alpha]_D -14.5^\circ$ , leading to a value of  $-39.1^\circ$  for the contained 3-methylcyclopentene, or an optical purity of 50%.<sup>19</sup>

Under similar experimental conditions, hydroboration of 3-ethylcyclopentene with (+)-diisopinocampheylborane, in the ratio of 2 to 1, gave (-)-3-ethylcyclopentene,  $[\alpha]_D -45.2^\circ$ , indicating an optical purity of 37%.<sup>20</sup>

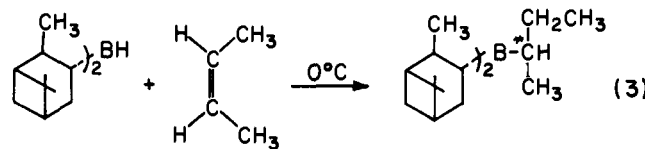
Hydroboration of racemic 1-methylnorbornene<sup>21</sup> with (+)-diisopinocampheylborane under the standard conditions yielded (-)-1-methylnorbornene,  $[\alpha]_D -6.5^\circ$ . Unfortunately, the rotation for the optically pure olefin is not available, so that the optical purity cannot be calculated. The organoborane produced was oxidized. Gas chromatographic analysis indicated the production of 12% of *exo*-1-methyl-2-norborneol and 88% of *exo*-1-methyl-3-norborneol.

Although these experiments were all carried out with (+)-diisopinocampheylborane from (-)- $\alpha$ -pinene, it is evident that the other enantiomer could be as readily obtained from the racemate by utilizing the reagent from (+)- $\alpha$ -pinene.

The results of these experiments are summarized in Table II.

## Discussion

**Asymmetric Synthesis of Organoboranes and Alcohols.**—In the reaction of optically active diisopinocampheylborane (or its dimer) with *cis*-2-butene there is produced an organoborane in which boron is attached to the asymmetric center of the 2-butyl group (3).



Oxidation produces 2-butanol in an optical purity of 87%. Since the  $\alpha$ -pinene utilized in these experiments is not better than 93 to 95% optically pure, this must mean that the hydroboration stage must involve an almost quantitative asymmetric synthesis, with the oxidation stage proceeding with essentially complete retention of configuration.

Such a complete asymmetric synthesis has hitherto not been known outside of enzymatic systems. It can only be the result of an unusually good fit in which the *cis*-2-butene readily adds to the reagent in one con-

(16) J. A. Berson and S. Suzuki, *J. Am. Chem. Soc.*, **81**, 4088 (1959), report  $[\alpha]_D +2.85$  to  $3.02^\circ$  (in chloroform) for *exo*-norborneol.

(17) K. Mislow and J. G. Berger, *ibid.*, **84**, 1956 (1962).

(18) G. Zweifel, N. R. Ayyangar, and H. C. Brown, *ibid.*, in press.

(19) M. Mousseron, R. Richaud, and R. Granger, *Bull. soc. chim. France*, 222 (1946), report  $[\alpha]_D +77.9^\circ$  for 3-methylcyclopentene.

(20) K. Mislow and I. V. Steinberg, *J. Am. Chem. Soc.*, **77**, 3807 (1955), report  $[\alpha]_D -123^\circ$  for 3-ethylcyclopentene.

(21) The olefin was a sample generously supplied by Professor Paul Schleyer of Princeton University.

TABLE II

PREPARATION OF OPTICALLY ACTIVE OLEFINS *via* HYDROBORATION OF RACEMIC OLEFINS WITH DIISOPINOCAMPHEYLBORANE AT 0°

Olefin	Olefin, mmoles	IPC <sub>2</sub> BH <sub>2</sub> <sup>a</sup> , mmoles	Rotation of recovered olefin, [α] <sub>D</sub> <sup>20</sup> , deg.	Optical purity, %	Yield of recovered olefin, %
3-Methylcyclopentene	62	31	-34.6	45	75
3-Methylcyclopentene	150	120	-50.8	65	
3- and 4-methylcyclopentene <sup>b</sup>	200	100	-14.5 <sup>c</sup>		
			-39.1 <sup>d</sup>	50	
3-Ethylcyclopentene	100	50	-45.2	37	80
1-Methylnorbornene	100	50	-6.5		67

<sup>a</sup> Diisopinocampheylborane from (-)-α-pinene. <sup>b</sup> A mixture of 37% 3- and 63% 4-methylcyclopentene. <sup>c</sup> Observed rotation for the recovered mixture. <sup>d</sup> Calculated for the 37% 3-methylcyclopentene in product.

formation, but adds only with great difficulty in the other possible conformation. Support for this view is provided by the observation that *trans*-2-butene and related olefins fail to add to diisopinocampheylborane in the same manner.<sup>18</sup> The addition stage with these olefins is very slow and proceeds predominantly with the displacement of α-pinene from the reagent. As a consequence, the remarkable stereospecificity observed in the reaction with the *cis*-olefins is lost.

The exceedingly high stereoselectivity of the reaction suggests the possibility of correlating the absolute configuration of the products with that of the reagent. Such a correlation has proved feasible<sup>6</sup> and will be discussed later in this paper.

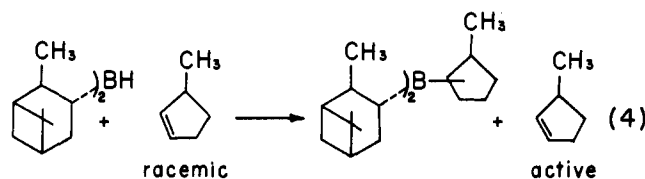
Another major point of interest resulting from the present study is the demonstration of boron having the capability of retaining asymmetry. Even when diisopinocampheyl-2-butylborane was permitted to stand at 25° for 48 hr. prior to oxidation, optical activity was retained to a large extent. The 2-butanol produced exhibited a rotation of +9.6°, in contrast to the value of +11.7° observed for material obtained for oxidation performed immediately following synthesis. Thus the very high optical purity which is realized upon immediate oxidation is not the only argument for the optical stability of such structures.

Reactive organometallics containing a metal to carbon bond at the asymmetric center are rare. Optically active 2-butylmercurials have been described,<sup>22,23</sup> but the carbon-mercury bond has long been recognized for its unusual stability.<sup>24</sup> In contrast, organolithium and organomagnesium compounds racemize too fast under ordinary conditions to permit their isolation as optically active derivatives.<sup>25-27</sup>

The present study has demonstrated that such asymmetric centers containing boron may be converted by alkaline hydrogen peroxide into alcohols with apparently complete retention of configuration. There is growing evidence that the preferred path for electrophilic substitutions involves retention.<sup>22,23</sup> Consequently, the ease with which organoboranes may be converted into other derivatives<sup>28</sup> with retention of configuration and the unusually high optical purity achieved should make this approach to optically active derivatives a most valuable one for synthetic organic chemistry.

**Separation of Optically Active Olefins.**—In view of the remarkably high stereoselectivity exhibited by

diisopinocampheylborane in its reactions with *cis*-olefins, it is not surprising that the reagent should also differentiate between the two enantiomers of a racemic pair of *cis*-olefins (4).



In the cases examined, the stereoselectivity was not as great as in the hydroboration of acyclic *cis*-olefins. Thus, treatment of 1-methylcyclopentene racemate with 50 mole % reagent yielded residual olefin of 45% optical purity, and use of 80 mole % reagent yielded residual product of 65% optical purity. Nevertheless, these are simple reactions to perform and provide conversions to products of reasonable optical purities in an area where such resolutions have been exceedingly difficult.<sup>29</sup>

It should be pointed out that since both enantiomers of α-pinene are readily available, it is practical to prepare both optical isomers of a given olefin with equal ease. Moreover, that portion of the olefin which reacts with the diisopinocampheylborane is not necessarily lost. In many instances it can be readily recovered from the organoborane by displacement with another olefin.<sup>30-32</sup> Since one of the two enantiomers reacts preferentially with the reagent, the olefin recovered by displacement should exhibit the opposite rotation of equal magnitude.

These considerations suggest that this simple resolution of olefin racemates should find a useful place in synthetic chemistry. It should be particularly valuable since, as shown in the following section, it is possible to predict the absolute configuration of the enantiomorph which reacts preferentially with the reagent, and thereby arrive at the configuration of the olefin which is recovered from the reaction mixture.

**Configurational Assignments for the Alcohols and Olefins Obtained *via* Hydroboration.**—The configurational relationship of (+)- and (-)-diisopinocampheylborane and their derivation from (-)- and (+)-α-pinene, respectively, was discussed in detail in an earlier paper.<sup>10</sup> Suffice it to say that the absolute configuration of α-pinene has been assigned<sup>33</sup> and diisopinocampheylborane appears to be formed by a simple *cis* addition of the borane molecule to the less hindered

(22) H. C. Chapman, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 2523 (1959).

(23) F. R. Jensen, L. D. Whipple, D. K. Wedegaertner, and J. A. Landgrebe, *J. Am. Chem. Soc.*, **81**, 1262 (1959).

(24) G. E. Coates, "Organometallic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1960, pp. 72-87.

(25) R. L. Letsinger, *J. Am. Chem. Soc.*, **72**, 4842 (1950).

(26) H. L. Goering and F. H. McCarron, *ibid.*, **80**, 2287 (1958).

(27) The successful preparation of an optically active Grignard reagent from (+)-1-bromo-1-methyl-2,2-diphenylcyclopropane was recently described: H. M. Walborsky and A. E. Young, *ibid.*, **83**, 2598 (1961).

(28) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, Chapter 3.

(29) Optically active stereoisomers of *trans*-cyclooctenes have been partially resolved recently by utilizing an olefin-optically active amine-platinum complex: A. C. Cope, C. R. Ganellin, and H. W. Johnson, *J. Am. Chem. Soc.*, **84**, 3191 (1962).

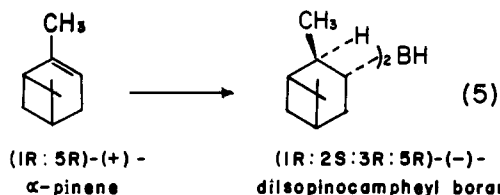
(30) R. Köster, *Ann.*, **618**, 31 (1958).

(31) H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **81**, 6434 (1959).

(32) H. C. Brown and M. V. Bhatt, *ibid.*, **82**, 2074 (1960).

(33) For a summary of the evidence and references dealing with the configuration of (+)-α-pinene see J. H. Brewster, *ibid.*, **81**, 5493 (1959).

side (away from the *gem*-dimethyl group) of the double bond<sup>34</sup> (5).

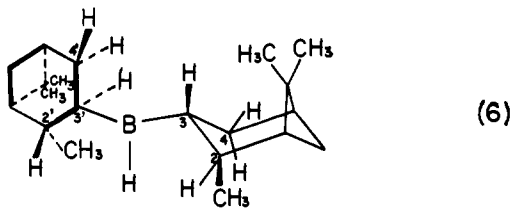


The configurations of the optically active alcohols and olefins obtained *via* hydroboration with (-)-diisopinocampheylborane exhibit a definite steric relationship to the configuration of the reagent. Consequently, it appears desirable to consider in detail the precise mechanism of the hydroboration stage in order to establish whether the model arrived at can account for the observed stereospecific syntheses which occur.

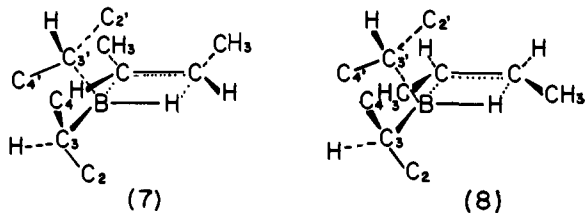
Although it is not yet certain whether the monomer or the dimer (*sym*-tetraisopinocampheylborane) is the actual hydroborating agent, the following discussion is referred to diisopinocampheylborane. However, this is not a decisive factor for the interpretation of the results. It should be understood that the correlation rules proposed below are formal and do not necessarily have mechanistic implications. However, since they serve to correlate the observed configurations in a considerable number of cases in both the alcohol and olefin syntheses, the correlation rules should be quite valuable in predicting the structures of products which have not yet been assigned absolute configurations.

To minimize possible confusion, the following discussion will be based only on (-)-diisopinocampheylborane, derived from (+)- $\alpha$ -pinene (5).

Inspection of models indicate that the most stable among the possible rotameric conformations for (-)-diisopinocampheylborane has a diequatorial arrangement of the borane group and the *trans*-methyl group in the adjacent position of the pinane moiety and an antiparallel or nearly antiparallel orientation of these two methyl groups in the two different pinane moieties. This leads to a probable description of the model for (-)-diisopinocampheylborane (6).



The addition of the boron-hydrogen bond to a double bond has been interpreted in terms of a four-center transition state.<sup>7</sup> The formation of such a highly rigid transition state should be strongly influenced by steric factors of both the reagent and the olefin. Thus the hydroboration of a *cis*-olefin, such as *cis*-2-butene, with diisopinocampheylborane can be represented by the two possible transition states, 7 and 8.

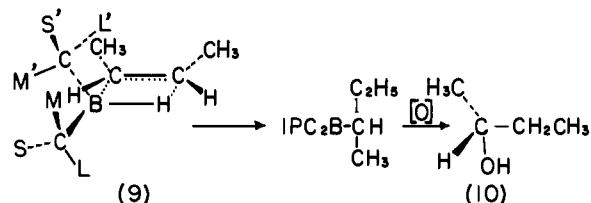


The model 6 shows that the boron atom is bonded to carbon atoms ( $C_3$  and  $C_3'$ ) carrying substituents of

(34) For the R-S configurational nomenclature, see R. S. Cahn, C. K. Ingold, and V. Prelog, *Experientia*, **12**, 81 (1956).

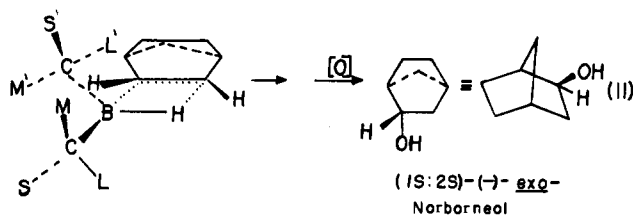
different size, namely a hydrogen atom at  $C_3'$  and a larger methylene group at  $C_4$ . It would, therefore, be anticipated that the preferred transition state would be that in which the methyl group of the *cis*-2-butene molecule is positioned away from the more bulky methylene group at  $C_4$  and toward the smaller hydrogen atom at  $C_3'$  (7). It is evident that the alternative transition state (8) will be less favorable sterically, with the bulky methyl group of the olefin and the methylene group at  $C_4$  in close proximity.

In order to simplify the model, the following symbols will be adopted, S (small) for hydrogen, M (medium) for methylene ( $C_4'$ ), and L (large) for the methyl group at  $C_2$  and  $C_2'$ .<sup>35</sup> On this basis, the preferred transition state 7, simplified to 9, will produce an organoborane which will be oxidized to (R)-(-)-2-butanol (10).

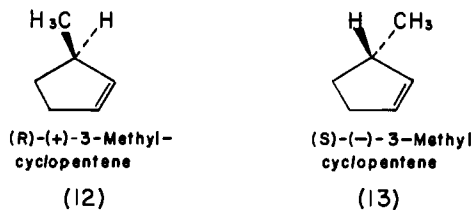


The same absolute configuration is predicted for all alcohols derived from the hydroboration of acyclic *cis*-olefins by (-)-diisopinocampheylborane, with the opposite configurations predicted for (+)-diisopinocampheylborane.

The addition of the boron-hydrogen bond to norbornene occurs from the *exo* direction. In order to attain an optimal steric fit, the norbornene must be orientated on the model as indicated in 11.



The enantiomeric 3-methylcyclopentenes have the configurations shown in 12 and 13.<sup>36</sup> For each enantiomer two possible transition states are conceivable;



the transition states for the R-olefin are represented by 14 and 15, those for the S-olefin by 16 and 17. The models indicate that transition states 14 and 16 should be nearly equally favorable. However, transition state 17 should be definitely more favorable than 15. Consequently, the S-enantiomer should react preferentially, leaving behind an excess of the R-olefin.

The addition of the boron-hydrogen bond to 1-methylnorbornene occurs from the *exo* direction. Consequently, only one transition state for each enantiomer need be considered. The configurations of the two enantiomers (1R:4S) and (1S:4R) are indicated in 18 and 19.

(35) This follows the practice introduced by Professors Cram and Prelog in their discussions of asymmetry syntheses: E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

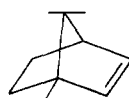
(36) J. H. Brewster, *J. Am. Chem. Soc.*, **81**, 5493 (1959).

TABLE III

CORRELATION OF CONFIGURATIONS OF ALCOHOLS AND OLEFINS OBTAINED *via* HYDROBORATION WITH (-)-DIISOPINOCAMPHEYLBORANE<sup>a</sup>

Olefin	Product	Configuration <sup>b</sup>	
		Predicted	Observed
<i>cis</i> -2-Butene	(-)-2-Butanol	R	R <sup>c</sup>
<i>cis</i> -2-Pentene	(-)-2-Pentanol	R	R <sup>c</sup>
<i>cis</i> -3-Hexene	(-)-3-Hexanol	R	R <sup>c</sup>
<i>cis</i> -4-Methyl-2-pentene	(-)-4-Methyl-2-pentanol	R	R <sup>c</sup>
Norbornene	(-)- <i>exo</i> -Norborneol	1S:2S	1S:2S <sup>d</sup>
Bicycloheptadiene	(+)- <i>exo</i> -Dehydronorborneol	1R:2S	1R:2S <sup>d</sup>
3-Methylcyclopentene	(+)-3-Methylcyclopentene	R	R <sup>e</sup>
3-Ethylcyclopentene	(+)-3-Ethylcyclopentene	R	R <sup>e</sup>
1-Methylnorbornene	(+)-1-Methylnorbornene	1S:4R	1S:4R <sup>f</sup>

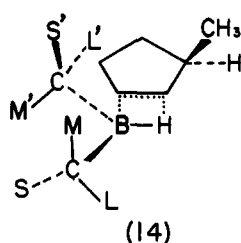
<sup>a</sup> From (+)- $\alpha$ -pinene. <sup>b</sup> The opposite configurations are realized from (+)-diisopinocampheylborane. <sup>c</sup> P. A. Levene and A. Rothen, *J. Org. Chem.*, 1, 75 (1936). <sup>d</sup> Ref. 17. <sup>e</sup> Ref. 36. <sup>f</sup> The configuration of (+)-1-methylnorbornene is not known. However, (-)-bornylene, which has a *gem*-dimethyl group at the 7-position, is related to (+)-camphor, since both give (+)-camphoric acid on oxidation. Consequently, (-)-bornylene has the (1S:4R) configuration. Assuming that the *gem*-dimethyl group does not affect the sign of rotation, (-)-1-methylnorbornene must have the (1R:4S) configuration, and consequently (+)-1-methylnorbornene the (1S:4R) configuration.



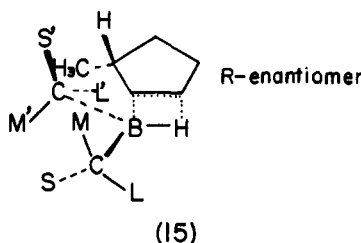
(1S:4R)-(-)-Bornylene



(1R:4S)-(-)-1-Methylnorbornene



(14)



(15)

R-enantiomer

should result in preferential reaction with the (1R:4S) enantiomer, leaving behind the less reactive (1S:4R) enantiomer.

The predicted and observed configurations are presented in Table III.

In all cases the observed result agrees with the absolute configuration predicted on the basis of the proposed model. It may, therefore, be concluded that the asymmetric syntheses *via* hydroboration with optically active diisopinocampheylborane should not only be helpful as a practical route to optically active derivatives, but it should also be valuable as a convenient means of establishing absolute configurations.

### Experimental

**Materials.**—Diglyme, tetrahydrofuran, and boron trifluoride etherate were purified as described earlier. The physical constants of the hydrocarbons used are given in Table IV.

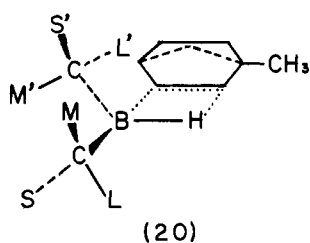
TABLE IV  
SUMMARY OF DATA FOR THE HYDROCARBONS UTILIZED

Hydrocarbon	B.p., °C.	M.p., °C.	$n_D^{20}$	Purity, %
<i>cis</i> -2-Butene				99
<i>cis</i> -2-Pentene			1.3832	99
<i>cis</i> -3-Hexene			1.3955	99
<i>cis</i> -4-Methyl-2-pentene			1.3900	95
3-Methylcyclopentene			1.4208	98
3-Ethylcyclopentene			1.4305	99
Norbornene		46-47		99
1-Methylnorbornene	104		1.4519	97
(+)- $\alpha$ -Pinene <sup>a</sup>			1.4660	
(-)- $\alpha$ -Pinene <sup>b</sup>			1.4660	

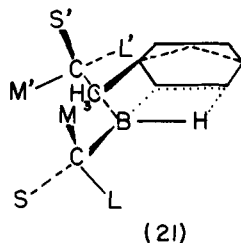
<sup>a</sup> The (+)- $\alpha$ -pinene was a sample distilled from French turpentine and was obtained from the Hercules Powder Co.;  $[\alpha]_D^{20} +47.6^\circ$ . <sup>b</sup> The (-)- $\alpha$ -pinene was prepared by the isomerization of (-)- $\beta$ -pinene and was purchased from the Glidden Co.;  $[\alpha]_D^{20} -47.9^\circ$ .

**Preparation of Diisopinocampheylborane.**—In a 300-ml. three-necked flask, equipped with a thermometer, condenser, pressure equalizing funnel, and a side arm capped with a rubber septum to permit removal of samples, was placed 0.20 mole of (+)- or (-)- $\alpha$ -pinene (27.2 g.) in 50 ml. of diglyme, and 75 ml. of a 1 M solution of sodium borohydride in diglyme. The flask was immersed in an ice bath. Diborane was generated by adding 12.6 ml. of boron trifluoride etherate (0.10 mole) diluted with 25 ml. of diglyme to the well stirred reaction mixture over a period of 15 min. (magnetic stirrer). During the boron trifluoride addition the diisopinocampheylborane precipitates. The reagent was maintained for an additional 4 hr. at 0° prior to its use. In cases where the ether interferes with gas chromatographic analysis

Hydroboration of these two enantiomers lead to the transition states, 20 and 21, respectively.



(20)



(21)

The model indicates that transition state 20, in which the methyl group of the olefin is pointed away from the pinane group, should be more favorable as compared with the alternative structure 21. Therefore, hydroboration with (-)-diisopinocampheylborane

for the olefins, the boron trifluoride etherate can be replaced by boron trifluoride diglymate.<sup>37</sup>

**Preparation of Optically Active Alcohols. (+)-2-Butanol in Diglyme.**—To a suspension of (+)-diisopinocampheylborane (0.10 mole) in diglyme at 0° was added 0.11 mole of *cis*-2-butene (6.1 g.). The reaction flask was equipped with a Dry Ice condenser in order to avoid losses of *cis*-2-butene. The reaction mixture was maintained for 4 hr. at 0°. Water was then added to decompose residual hydride. The organoborane was oxidized at 30–40° by adding 32 ml. of 3 *N* sodium hydroxide followed by dropwise addition of 32 ml. of 30% hydrogen peroxide. After stirring for an additional hour, the alcohols formed were extracted with ether. The ether extract was washed once with a solution of saturated sodium chloride, then dried over anhydrous magnesium sulfate. The ether was removed and the alcohol distilled through a glass spiral column. There was obtained 6.2 g. of 2-butanol (83% yield), b.p. 98° at 752 mm.,  $n_D^{20}$  1.3970,  $[\alpha]_D^{20} + 11.7^\circ$ , indicating an optical purity of 86%.<sup>12</sup>

The residue was diluted with ether, and the ether was washed with cold water to remove diglyme. There was obtained 28.2 g. of isopinocampheol (91% yield), m.p. 55–56°,  $[\alpha]_D^{20} + 32^\circ$  (*c* 4, benzene); lit.<sup>38</sup> for (–)-isopinocampheol, m.p. 54–56°,  $[\alpha]_D^{20} - 32.4^\circ$  (*c* 4, benzene).

Similarly, hydroboration of *cis*-2-butene with (–)-diisopinocampheylborane gave after oxidation a 90% yield of (–)-2-butanol, b.p. 98° at 744 mm.,  $n_D^{20}$  1.3975,  $[\alpha]_D^{20} - 11.8^\circ$ , an optical purity of 87%.

**(+)-2-Butanol in Tetrahydrofuran.**—In a 300-ml. flask was placed 29.9 g. of (–)- $\alpha$ -pinene (0.22 mole, 10% excess) and 60 ml. of tetrahydrofuran. The flask was immersed in an ice bath. To the olefin was added 56 ml. of a 1.77 *M* solution of borane (0.10 mole of  $BH_3$ ) in tetrahydrofuran. The reaction mixture was stirred for 4 hr. at 0°, then was diluted with 6.1 g. of *cis*-2-butene (0.11 mole). The reaction was maintained for 4 hr. at 0°. Excess hydride was decomposed by adding 5 ml. of water. The organoborane was oxidized by adding 32 ml. of 3 *N* sodium hydroxide, followed by dropwise addition of 32 ml. of 30% hydrogen peroxide. The alcohols formed were extracted with ether. The residue obtained after removal of the solvents was distilled. There was obtained 6.3 g. of (+)-2-butanol,  $[\alpha]_D^{20} + 10.5^\circ$ , indicating an optical purity of 78%.

**(–)-3-Hexanol.**—To a suspension of (–)-diisopinocampheylborane (0.10 mole) in diglyme at 0° was added 8.4 g. of *cis*-3-hexene (0.10 mole). The reaction flask was maintained for 4 hr. at 0°. The reaction mixture was diluted with water (5 ml.), then oxidized with alkaline hydrogen peroxide as described above. The alcohol formed was extracted with ether, and the ether extract was washed carefully with cold water to remove diglyme. The 3-hexanol obtained after distillation had b.p. 135–136° at 752 mm.,  $n_D^{20}$  1.4148,  $[\alpha]_D^{20} - 6.5^\circ$ , indicating a 91% optical purity.<sup>13</sup>

**(+)-2-Pentanol.**—Hydroboration of 7.0 g. of *cis*-2-pentene (0.10 mole) with (+)-diisopinocampheylborane (0.10 mole) in diglyme, followed by oxidation with alkaline hydrogen peroxide (32 ml. of 3 *N* sodium hydroxide and 32 ml. of 30% hydrogen peroxide), gave a mixture of 2- and 3-pentanol. Gas chromatographic analysis on a glycerol column indicated 70% 2- and 30% 3-pentanol. The mixture was purified by gas chromatography using a glycerol column. There was obtained a 76:24 mixture of 2- and 3-pentanol,  $n_D^{20}$  1.4063,  $[\alpha]_D^{20} + 8.6^\circ$ . Since 3-pentanol is optically inactive, the calculated optical purity amounts to 82%.<sup>14</sup>

**(+)-4-Methyl-2-pentanol.**—*cis*-4-Methyl-2-pentene (8.4 g., 0.10 mole) was hydroborated with (+)-diisopinocampheylborane (0.10 mole) as described above. The organoborane was oxidized with alkaline hydrogen peroxide, and the alcohols formed were extracted with ether. Analysis of the dried ether extract by gas chromatography on a glycerol column revealed 92% of 4-methyl-2-pentanol and 8% of 2-methyl-3-pentanol. Evaporation of the ether, followed by distillation of the residue, gave a distillate (b.p. 131–132° at 751 mm.), which was further purified by gas chromatography on a glycerol column. The 4-methyl-2-pentanol thus obtained was 96% pure,  $n_D^{20}$  1.4115,  $[\alpha]_D^{20} + 16.0^\circ$ , indicating an optical purity of 76%.<sup>15</sup>

**(+)-*exo*-Norborneol.**—Freshly sublimed norbornene (9.4 g., 0.10 mole, m.p. 46–47°) was hydroborated with (+)-diisopinocampheylborane (0.10 mole) in diglyme. The organoborane was oxidized at 30–40°, and the alcohol formed was extracted with ether. The ether extract was washed with ice-water to remove diglyme, then dried. The residue obtained after removal of the ether (cold finger) was diluted with 10 ml. of *n*-decane. The *exo*-

norborneol codistilled with *n*-decane at 158–163°, using a glass spiral column. Fractions of approximately 5 ml. were collected. At the end of the distillation an additional 10 ml. of *n*-decane was added and the distillation was continued. In all, 50 ml. of *n*-decane was used and ten fractions were collected. The *exo*-norborneol crystallized by keeping the fractions at 0 to –6°. The crystalline product was collected. There was obtained 62% of *exo*-norborneol, which after recrystallization from a small amount of *n*-pentane had m.p. 125–126°,  $[\alpha]_D^{20} + 1.95^\circ$  (*c* 3,  $CH_2Cl_2$ ), indicating a 65–68% optical purity.<sup>16</sup>

Similarly, (–)-*exo*-norborneol was obtained by the hydroboration of norbornene with (–)-diisopinocampheylborane. The pure alcohol had m.p. 125–126°,  $[\alpha]_D^{20} - 2.0^\circ$  (*c* 3,  $CH_2Cl_2$ ), acetate  $\alpha_D^{20} + 7.9^\circ$  (1 dm.), indicating an optical purity of 67–70%.

**Preparation of Optically Active Olefins. (–)-3-Methylcyclopentene.**—To a suspension of (+)-diisopinocampheylborane (31 mmoles) in diglyme at –15° was added 5.11 g. of racemic 3-methylcyclopentene (62 mmoles). The reaction mixture was stirred for 4 hr. at 0°. Water was added to decompose any residual hydride (1 ml.). The unreacted 3-methylcyclopentene was recovered from the reaction mixture by distillation at 0–20° at reduced pressure (1 to 2 mm.). The olefin was collected in a cold trap (–78°), dried, and redistilled. There was obtained 1.91 g. of 3-methylcyclopentene (75% yield), b.p. 63–64° at 750 mm.,  $n_D^{20}$  1.4205,  $[\alpha]_D^{20} - 34.6^\circ$ , an optical purity of 45%.<sup>19</sup>

The residual organoborane was oxidized with alkaline hydrogen peroxide. The alcohols formed (methylcyclopentanols and isopinocampheol) were extracted with ether. The ether extract was oxidized with chromic acid–sulfuric acid.<sup>39</sup> Gas chromatographic analysis for ketones on a Ucon polar column revealed 30% of 2-methylcyclopentanone and 70% of 3-methylcyclopentanone.

A higher optical purity of 3-methylcyclopentene is realized when more than 50 mole % of the racemic olefin is hydroborated. Thus, hydroboration of 0.15 mole of 3-methylcyclopentene with 0.12 mole of (+)-diisopinocampheylborane gave an 80% yield of 3-methylcyclopentene,  $n_D^{20}$  1.4206,  $[\alpha]_D^{20} - 50.8^\circ$ , indicating a 65% optical purity.

**(–)-3-Methylcyclopentene from a Mixture of 3- and 4-Methylcyclopentene.**—A 37:63 mixture of 3-methyl- and 4-methylcyclopentene (0.20 mole) was hydroborated with 0.10 mole of (+)-diisopinocampheylborane. At the end of the reaction, gas chromatographic analysis indicated no change in the composition of the olefin mixture. The excess olefin was distilled from the reaction mixture under reduced pressure. There was obtained 8.1 g. of distillate,  $n_D^{20}$  1.4207,  $[\alpha]_D^{20} - 14.5^\circ$ . Since 4-methylcyclopentene is optically inactive, the calculated rotation for 3-methylcyclopentene is  $[\alpha]_D^{20} - 39.1^\circ$ , indicating a 50% optical purity.

**(–)-3-Ethylcyclopentene.**—Under similar experimental conditions as described above, racemic 3-ethylcyclopentene (0.10 mole) was added to a suspension of (+)-diisopinocampheylborane (50 mmoles). The unreacted 3-ethylcyclopentene was recovered from the reaction mixture by distillation at reduced pressure. Redistillation gave 80% of 3-ethylcyclopentene, b.p. 99° at 745 mm.,  $n_D^{20}$  1.4305,  $[\alpha]_D^{20} - 45.2^\circ$ , indicating a 37% optical purity.<sup>20</sup>

**(–)-1-Methylnorbornene.**—Racemic 1-methylnorbornene (10.8 g., 0.10 mole) was hydroborated with (+)-diisopinocampheylborane (50 mmoles) at 0°. The excess olefin was distilled from the reaction mixture at 20° under reduced pressure (1 to 2 mm.). There was obtained 3.8 g. of 1-methylnorbornene, b.p. 104° at 740 mm.,  $n_D^{20}$  1.4515,  $[\alpha]_D^{20} - 6.51^\circ$  (lit.<sup>40</sup> b.p. 104°,  $n_D^{20}$  1.4519).

The residual organoborane was oxidized in the usual way. The reaction mixture was extracted with ether, and the dried ether extract was analyzed by gas chromatography on a Carbowax-20M column for isomeric alcohols. The chromatogram revealed 12% of *exo*-1-methyl-2-norborneol and 88% of *exo*-1-methyl-3-norborneol.

**Acknowledgment.**—We are greatly indebted to Professor Paul Schleyer of Princeton University for the sample of 1-methylnorbornene, to Dr. R. A. Bankert of the Hercules Powder Co., Wilmington, Del., for a generous gift of (+)- $\alpha$ -pinene distilled from French turpentine, and to the Glidden Co., Jacksonville, Fla., for converting a large sample of (–)- $\beta$ -pinene into (–)- $\alpha$ -pinene.

(37) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 1241 (1961).

(38) H. Schmidt, *Ber.*, **77**, 544 (1944).

(39) H. C. Brown and C. P. Garg, *J. Am. Chem. Soc.*, **83**, 2952 (1961):

(40) P. Schleyer, Abstracts of Papers, 130th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1956, p. 29.