phoresis of the reaction mixture at pH 7.5 showed little of inorganic trimetaphosphate (XX). Subsequent heating of the pyridine mixture at 100° for 0.5 hr. gave a product in about 50% yield identical in mobility on paper electrophoresis with authentic inorganic trimetaphosphate. The latter was clearly separated from inorganic pyrophosphate, linear triphosphate and orthophosphate.

In another experiment 60 mg. of monobenzyl phosphoric acid was treated with DCC (135 mg.) in 2 ml. of dry acetonitrile for 0.5 hr., and to the reaction mixture was added a solution of sodium iodide (300 mg.) in acetonitrile (2 ml.). Subsequent heating of the reaction mixture at 55° for 30 min. again gave inorganic trimetaphosphate in about 50% yield.

COMMUNICATIONS TO THE EDITOR

DIISOPINOCAMPHEYLBORANE AS A REAGENT FOR THE PRODUCTION OF OPTICALLY ACTIVE OLEFINS AND THE ESTABLISHMENT OF THEIR CONFIGURATION

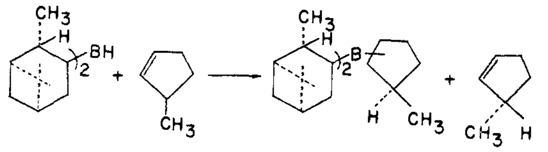
Sir:

It has been reported recently that the optically active stereoisomers of *trans*-cycloöctenes can be isolated by utilizing an olefin amine platinum complex.[1] We wish to report that the partial hydroboration of a racemic mixture of olefins by diisopinocampheylborane provides a highly convenient means for the isolation of the individual optically active isomers. Moreover, the method permits one to assign the absolute configuration to the products.

It was observed previously that diisopinocampheylborane exhibits a remarkable asymmetric stereoselectivity when applied to the hydroboration of *cis*-olefins[2] and to the reduction of ketones.[3] Thus, hydroboration of *cis*-olefins with the reagent, and then oxidation of the intermediate organoborane, yielded alcohols in optical purities of 70–90%. The configuration of the alcohols obtained can be rationalized in terms of an optimal steric fit of the reagent involved in the transition state.[4]

Inspection of models indicates that the asymmetric reagent should differentiate between enantiomeric olefins. Accordingly, hydroboration of an olefin racemate with a deficient amount of diisopinocampheylborane should result in an accumulation of one enantiomer in the reaction mixture as a consequence of the more reactive enantiomer being converted into the organoborane.

For example, on the basis of the model, one would predict that the R enantiomer of 3-methylcyclopentene should react more readily with diisopinocampheylborane derived from (−)α-pinene, leaving an excess of the S enantiomer.

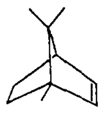


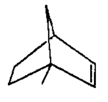
racemic active

In a typical esperiment 8.47 g. of α-pinene (62 mmoles, $[\alpha]^{20}\text{D}$ −47.8°) was added to 23.4 ml. of a 1.0 *M* solution of sodium borohydride in diglyme. Boron trifluoride, 8.5 ml. of 3.65 *M* solution in diglyme, was added to the olefin–sodium borohydride mixture. The flask was maintained for 4 hours at 0–5°. The diisopinocampheylborane thus obtained (32 mmoles) was treated with 5.08 g. of 3-methylcyclopentene (62 mmoles). The reaction was permitted to proceed for 4 hours at 0–5°. Water was added to decompose residual hydride. The unreacted 3-methylcyclopentene was recovered from the reaction mixture by distillation at 0–20° at reduced pressure. Redistillation yielded 1.91 g. of 3-methylcyclopentene (75% yield), b.p. 63–64° at 750 mm., $n^{20}\text{D}$ 1.4205, $[\alpha]^{26}\text{D}$ − 34.6°, indicating an optical purity of 45%.[5] (−)3-Methylcyclopentene has the S configuration,[6] in agreement with the prediction.

Under similar experimental conditions racemic 3-ethylcyclopentene yielded 80% of optically active 3-ethylcyclopentene, b.p. 99–99.5° at 765 mm., $n^{20}\text{D}$ 1.4305, $[\alpha]^{26}\text{D}$ −45.2°, indicating an optical purity of 37%.[7] The (−)enantiomer has the S configuration[6] which is in agreement with the one deduced from inspection of models.

Similarly, partial hydroboration of racemic 1-methylnorbornene yielded optically active 1-methylnorbornene in 67% yield, b.p. 104–105° at 760 mm., $n^{20}\text{D}$ 1.4513[8], $[\alpha]^{26}\text{D}$ −6.51°. The configuration of (−)1-methylnorbornene is not known. However, (−)bornylene, which has a *gem* dimethyl group at the bridge carbon atom, 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.


(−) Bornylene
1S:4R


1-Methylnorbornene
1R:4S

Inspection of models predicts the same configuration for the 1-methylnorbornene obtained by selective hydroboration with the diisopinocampheylborane from (−)α-pinene.

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[1] A. C. Cope, C. R. Ganellin and H. W. Johnson, Jr., *J. Am. Chem. Soc.*, **84**, 3191 (1962).

[2] H. C. Brown and G. Zweifel, *ibid.*, **83**, 486 (1961).

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

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

[5] M. Mousseron, R. Richaud and R. Granger, *Bull. soc. chim. France*, 222 (1946), report for 3-methylcyclopentene, $[\alpha]_{5790}$ +77.9°.

[6] J. H. Brewster, *J. Am. Chem. Soc.*, **81**, 5493 (1959).

[7] K. Mislow and I. V. Steinberg, *ibid.*, **77**, 3807 (1955), report for 3-ethylcyclopentene $[\alpha]\text{D}$ −123°.

[8] P. v. R. Schleyer, "Abstracts of Papers, A.C.S.," Sept., 1956, p. 29, reports b.p. 104.3°, $n^{22}\text{D}$ 1.4519.

Since (+)α-pinene is also available, the procedure makes it possible to obtain both of the optically active isomeric olefins.

Hydroboration of more than 50 mole per cent of a *dl* olefin with diisopinocampheylborane, should leave behind an olefin with increased optical purity. Indeed, when 150 mmoles of 3-methylcyclopentene was hydroborated with 120 mmoles of diisopinocampheylborane (derived from (−)α-pinene), it was found that the excess 3-methylcyclopentene was 65% optically pure with $[\alpha]^{26}_{D}$ −50.8°.

Acknowledgment.—We wish to acknowledge the assistance provided by the National Science Foundation (G 19878), and by Professor P. v. R. Schleyer for the sample of 2-methylnorbornene.

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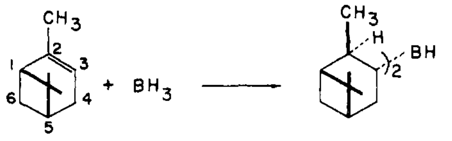
RECEIVED SEPTEMBER 20, 1962

HYDROBORATION AS A MEANS FOR THE ASSIGNMENT OF CONFIGURATIONS TO ALCOHOLS AND OLEFINS

Sir:

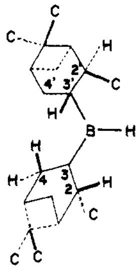
We wish to report a new method for configurational assignment based on the hydroboration reaction. Thus, the configuration of alcohols and olefins derived from the hydroboration of a number of representative *cis*-olefins with diisopinocampheylborane can be successfully deduced by considering the steric course of the reaction.

Hydroboration of (+)α-pinene[1,2] (I) with diborane occurs *cis* and from the rear side of the olefin to yield (+) diisopinocampheylborane[3,4] (II). Inspection of models indicates that the most stable among the rotameric conformations for diisopinocampheylborane has (a) a diequatorial arrangement of the CH_3– and borane group in the pinane moiety, and (b) an *anti-* or nearly *anti-parallel* orientation of the CH_3– groups in the two pinane moieties. This leads to an unambiguous description of the model for (+) diisopinocampheylborane (III).

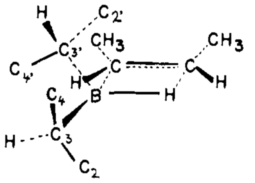


I II

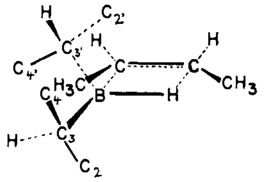
The addition of the boron–hydrogen bond to a double bond has been interpreted in terms of a four-center transition state.[3] The formation of such a highly rigid transition state should be strongly influenced by the steric factors of both the reagent and the olefin. Thus, the hydroboration of an olefin, such as *cis*-2-butene, with diisopinocampheylborane can be represented by transition states IV and V.



III



IV



V

The model (III) shows that the boron atom is bonded to carbon atoms (C_3 and C_3') carrying substituents of different size, namely, a bulky methylene group (C_4) and a hydrogen atom (at C_3'). The preferred transition state is therefore the one in which the methyl group of the olefin is positioned away from the bulky methylene group (C_4) and toward the smaller hydrogen atom (at C_3') of the diisopinocampheylborane reagent (IV). It is evident that the alternative transition state (V) will be much less favorable sterically with the bulky methyl group of the olefin and the methylene group at C_4 in close proximity. The 2-butanol obtained after oxidation, a reaction which occurs with retention of the configuration,[3] will have the R configuration.[2] *The same configuration is predicted for all alcohols derived from the hydroboration of acyclic cis-olefins.*

The addition of the boron–hydrogen bond to norbornene occurs from the *exo*-side.[3] In order to obtain an optimal steric fit, the norbornene has to be orientated on the model in the same way as *cis*-2-butene.

TABLE I

CORRELATION OF CONFIGURATIONS OF ALCOHOLS AND OLEFINS *via* HYDROBORATION WITH DIISOPINOCAMPHEYLBORANE

		Configuration[a]	
Olefin	Product formed	Predicted	Found
cis-2-Butene	(−) 2-Butanol	R	R
cis-2-Pentene	(−) 2-Pentanol	R	R
cis-3-Hexene	(−) 3-Hexanol	R	R
cis-4-Methyl-2-pentene	(−) 4-Methyl-2-pentanol	R	R
Norbornene	(−) *exo*-Norbornenol	2S	2S
3-Methylcyclopentene	(+) 3-Methylcyclopentene	R	R
3-Ethylcyclopentene	(+) 3-Ethylcyclopentene	R	R
1-Methylnorbornene	(+) 1-Methylnorbornene	1S:4R	1S:4R

s Configuration predicted and found based on the use of (+)α-pinene with configuration 1R:5R. The opposite configurations are realized by the use of (−)α-pinene with configuration 1S:5S.

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(1) For a summary of the evidence (and references) dealing with the configuration of (+)α-pinene see: J. H. Brewster, *J. Am. Chem. Soc.*, **81**, 5493 (1959). Structure I shows (+)α-pinene with absolute configuration 1R:5R.

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

(3) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 2544 (1961).

(4) Although it is not certain whether the monomer or the dimer (*sym*-tetraisopinocampheyldiborane) is the actual hydroborating agent, the following discussion is referred to the monomeric form. However, this is not a decisive factor for the interpretation of the results obtained in the present study.