Table II

| Compound | Formula | Bp, °C (mm) | $n^{25}D$ | C, % Calcd | C, % Found | H, % Calcd | H, % Found | F, % Calcd | F, % Found | S or N, % Calcd | S or N, % Found |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *p*-$FC_6H_4CH_2$–$CH_2$ | $C_9H_9F$ | 90(45) | 1.5051 | 79.38 | 79.71 | 6.66 | 7.00 | 13.95 | 13.30 | | |
| *m*-$FC_6H_4CH_2$–$CH_2$ | $C_9H_9F$ | 85(40) | 1.5049 | 79.38 | 79.84 | 6.66 | 6.71 | 13.95 | 13.0 | | |
| *p*-$FC_6H_4CH_2$–$CH_2$ | $C_8H_7FO$ | 92(14) | 1.5074 | 69.56 | 69.94 | 5.11 | 4.68 | 13.75 | 13.5 | | |
| *m*-$FC_6H_4CH_2$–$CH_2$ | $C_8H_7FO$ | 89(13) | 1.5078 | 69.56 | 69.95 | 5.11 | 5.41 | 13.75 | 13.3 | | |
| *p*-$FC_6H_4CH_2$–$CH_2$ | $C_8H_7FS$ | 52–56(0.5) | 1.5610 | 62.31 | 63.08 | 4.58 | 4.97 | 12.32 | 12.5 | 20.75 | 19.47 |
| *m*-$FC_6H_4CH_2$–$CH_2$ | $C_8H_7FS$ | 60–65(1–2) | 1.5601 | 62.31 | 63.02 | 4.58 | 4.72 | 12.32 | 13.4 | 20.75 | 19.10 |
| *p*-$FC_6H_4CH_2$–$CH_2$ | $C_8H_8FN$ | 132–138(6–8) | 1.5310 | 70.05 | 69.38 | | | 13.85 | 14.5 | 10.22 | 10.15 |
| *m*-$FC_6H_4CH_2$–$CH_2$ | $C_8H_8FN$ | 127–129(6) | 1.5330 | 70.05 | 69.93 | | | 13.85 | 14.0 | 10.22 | 9.81 |
| *p*-$FC_6H_4C(=O)NCH_3$[a] | $C_8H_8FON$ | 45(0.05) | 1.5080 | 62.74 | 62.85 | 5.24 | 4.98 | | | | |
| *m*-$FC_6H_4C(=O)NCH_3$[a] | $C_8H_8FON$ | 45(0.05) | 1.5076 | 62.74 | 62.24 | 5.24 | 5.41 | | | | |

[a] Active oxygen by iodometric analysis was >90%.

magnetic resonance spectrum. The chemical shift of the aliphatic protons were found in every case to be identical with that observed in the spectrum of the corresponding nonfluorinated compound.

**Procedure.** Fluorine nmr spectra were obtained with Varian Associates high-resolution nmr spectrometer operating at 56.4 Mcps. Approximately 5% (volume) solutions of the fluorobenzenes were used with either 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane or *o*-difluorobenzene as the internal reference. The chemical shifts were then related to fluorobenzene as described previously.[18]

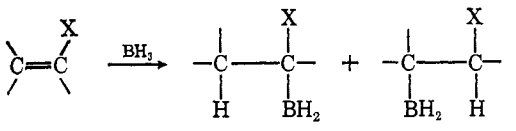
# Transfer Reactions Involving Boron. XIV. The Stereochemistry of $\alpha$-Transfer Reactions[1]

**Daniel J. Pasto and James Hickman**[2]

*Contribution from the Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556.* *Received April 21, 1967*

**Abstract:** The stereochemistry of the rearrangement of $\alpha$-chloroorganoboranes, formed in part in the hydroboration of vinyl chlorides, to alkylchloroboranes is shown to proceed with complete inversion of stereochemistry at carbon.

The addition of borane to a heterosubstituted olefin (**1**) results in the formation of both $\alpha$- and $\beta$-heterosubstituted organoboranes (**2** and **3**, respectively), the relative amounts of the two isomers depending on the heterofunctional group X. Previous investigations in our laboratories have shown that **2** undergoes spontaneous rearrangement to **4**,[3-5] termed an $\alpha$ transfer,[3]



(1)

**1** **2** **3**

that this rearrangement occurs prior to the basic oxidation–hydrolysis work-up procedure, and that **2** does

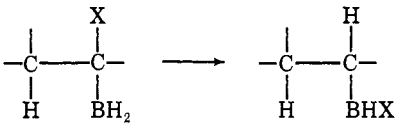
(1) Part XIII: D. J. Pasto, J. Chow, and S. K. Arora, *Tetrahedron Letters*, 723 (1967).

(2) Reilly Research Fellow, 1965–1966; National Institutes of Health Predoctoral Fellow (1-F1-GM-31, 055-01A1), 1966 to present.

(3) D. J. Pasto and J. L. Miesel, *J. Am. Chem. Soc.*, **85**, 2118 (1963).

(4) D. J. Pasto and C. C. Cumbo, *ibid.*, **86**, 4343 (1964).

(5) D. J. Pasto and R. Snyder, *J. Org. Chem.*, **31**, 2773 (1966).



(2)

2 4

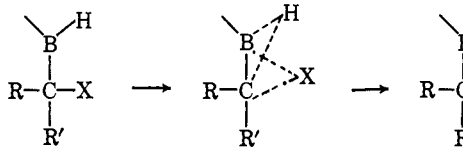
not give rise to olefinic intermediates (*via* carbene intermediates). Intermediates of type **3** may undergo a spontaneous *cis* elimination (X = OR),[4] base- (tetrahydrofuran) catalyzed *trans* eliminations (X = Cl, Br),[5] or $\beta$-transfer reactions (eq 3, X= SR and OR).[3,4]

(3)

3

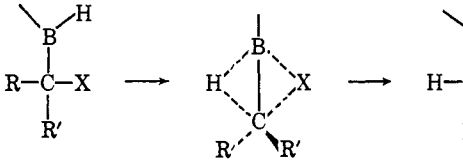
In a recent study in our laboratories on the mechanism of product formation in the hydroboration of vinyl halides,[5] it was concluded that intermediates of type **2** (X = Cl, Br) do not give rise to carbene intermediates capable of undergoing intramolecular insertion or rearrangement to olefins. However, the experimental evidence did not allow us to determine if the rearrangement illustrated in eq 2 proceeds *via* a carbene complex **5**. Three possible mechanisms were proposed for the rearrangement illustrated in eq 2:[5] (1) rearrangement *via* an "electrophilic substitution" type transition state leading to retention of configuration at carbon (eq 4); (2) rearrangement *via* a "nucleophilic substitution" transition state leading to inversion of configuration at carbon (eq 5); and (3) rearrangement *via* a carbene complex **5** leading to the loss of stereochemistry at carbon (eq 6).

Electrophilic transition state



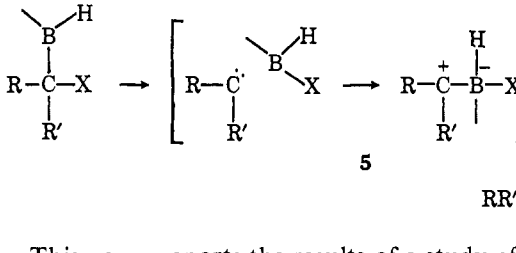
(4)

Nucleophilic transition state



(5)

*Via* carbene complex



5

(6)

This paper reports the results of a study of the stereochemistry of the rearrangement illustrated in eq 1 (X = Cl) which strongly favors the "nucleophilic substitution" type transition state illustrated in eq 5.

## Results and Discussion

The synthesis of intermediates of type **2** cannot be accomplished at the present time by means other than the hydroboration of the heterosubstituted olefins **1**. Thus the chemistry of intermediates of structure **2** is difficult to unravel due to the simultaneous formation of the $\beta$ derivatives **3** which are themselves very reactive intermediates. Fortunately, it is possible to select systems which favor the formation of type **2** intermediates and which allow distinction between the chemistry of the two hydroboration intermediates. The hydroboration of vinyl halides leads to the predominant formation of type **2** intermediates and were thus selected for this study. Distinction between the chemistry of intermediates **2** and **3**, and the determination of the stereochemistry of the ensuing rearrangement of **2**, can be followed by incorporating stereochemical or labeling handles in the formation of the intermediates **2** and **3**.

The hydroboration of 2-methylchlorocyclohexene (**6**) is expected to give rise to the two adducts **7** and **8** (see Figure 1). The *trans*-$\beta$-chloro adduct **8** would be expected to undergo a solvent catalyzed $\beta$-elimination[5,6] to give 1-methylcyclohexene (**9**). The 1-methylcyclohexene would undergo immediate hydroboration[7] giving, after basic hydrogen peroxide oxidation, a mixture of *trans*-2-methylcyclohexanol and 1-methylcyclohexanol.

The $\alpha$-chloro adduct **7** may undergo rearrangement[8] with inversion (*via* eq 5) to give **10** and subsequently *cis*-2-methylcyclohexanol, with retention (*via* eq 4) to give **11** and subsequently *trans*-2-methylcyclohexanol, or *via* a carbene complex (eq 6) to give an expected mixture of **10** and **11** and thus a mixture of the *cis*- and *trans*-2-methylcyclohexanols. As the 1-methylcyclohexanol can be formed only by hydroboration of 1-methylcyclohexene,[9] this product serves as an internal handle capable of distinguishing between the three possible modes of reaction of the $\alpha$-chloro adduct **7**. For example, rearrangement of **7** exclusively *via* the inversion mechanism does not produce any *trans*-2-methylcyclohexanol, and thus the *trans*-2-methylcyclohexanol to 1-methylcyclohexanol ratio will be that obtained by hydroboration of 1-methylcyclohexene,[10] observed to be 11.5:1 in an independent control experiment. Rearrangement of **7** exclusively *via* the retention mechanism (eq 4) will result in a mixture of *trans*-2-methylcyclohexanol and 1-methylcyclohexanol *only* in a ratio greater than 11.5:1. Rearrangement of **7** *via* the carbene complex will yield a mixture of *cis*- and *trans*-2-methylcyclohexanol and 1-methylcyclohexanol in which the ratio of the latter two will be greater than 11.5:1.

Experimentally the hydroboration of compound **6** at 0° in diglyme employing an olefin:borane mole ratio of

(6) D. J. Pasto and R. Snyder, *J. Org. Chem.*, **31**, 2777 (1966).

(7) Simple alkenes undergo hydroboration at a faster rate than the haloolefins[5] and thus even in the presence of **6** preferential hydroboration of 1-methylcyclohexene will occur.

(8) The $\alpha$-chloro adduct **7** does not give rise to 1-methylcyclohexene, or 3-methylcyclohexene, by rearrangement of a possible 2-methylcyclohexyl carbene intermediate, as evidenced by our earlier studies[5] and the absence of the expected 3-methylcyclohexanols, derived by the hydroboration of 3-methylcyclohexene, in the present study.

(9) $\beta$-Transfer reactions involving *trans*-$\beta$-substituted organoboranes have not been observed to occur.[4,5]

(10) A complication arises in that 1-methylcyclohexene may be hydroborated either by borane or monochloroborane, formed in the *trans*-$\beta$-elimination. It has been shown in an independent study that hydroborations using monochloroborane are much slower than with borane[11] and thus the intermediate 1-methylcyclohexene will be selectively hydroborated by borane and not the monochloroborane.

(11) D. J. Pasto and P. Balasubramaniyan, *J. Am. Chem. Soc.*, **89**, 295 (1967).

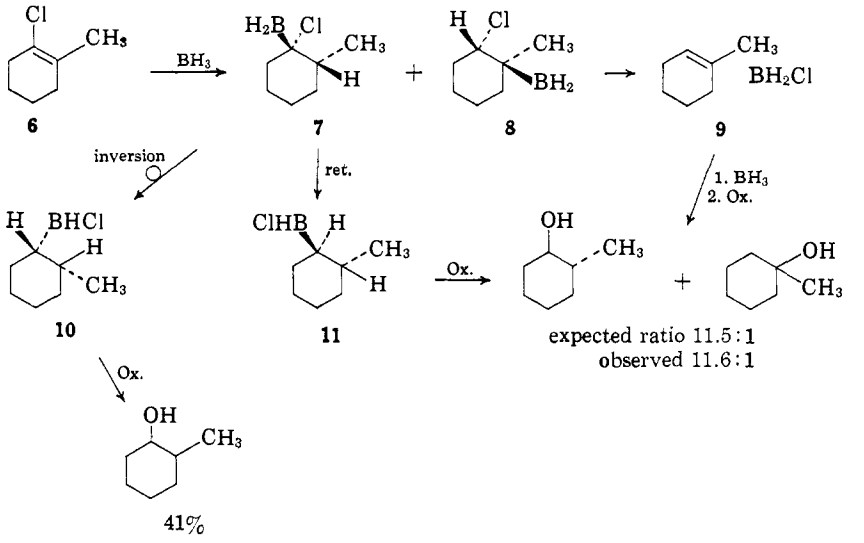



Figure 1. Products formed in the hydroboration of 1-chloro-2-methylcyclohexene (**6**).

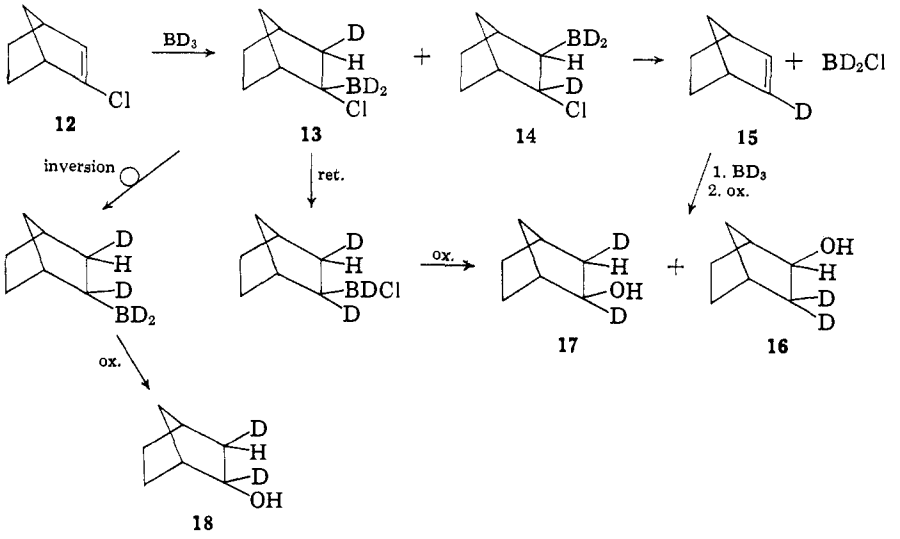



Figure 2. Products formed in the deuterioboration of 2-chloronorbornene (**12**).

1:1 yields 41.1% *cis*-2-methylcyclohexanol, 31.3% *trans*-2-methylcyclohexanol, 2.7% 1-methylcyclohexanol, and a trace of 1-methylcyclohexene. The experimentally observed ratio of *trans*-2-methylcyclohexanol to 1-methylcyclohexanol is 11.6:1, well within the limit of experimental error of the analysis. *The rearrangement of* **7** *must therefore occur with 100% inversion.* Identical results are obtained using *m*-chloroperbenzoic acid as the oxidant[5] precluding the fact that the rearrangement occurred during the basic oxidation procedure.

Similar results are derived from the deuterioboration of 2-chlorobornene (**12**). Addition of perdeuterioborane to 2-chloronorbornene is expected to give only the adducts **13** and **14**[12] (see Figure 2). The *trans*-β-chloro adduct **14** may undergo a tetrahydrofuran-catalyzed *trans*-β-elimination[13] to give 2-deuteronorbornene (**15**), which on subsequent deuterioboration and oxidation will give equal amounts (based on ignoring any deuterium isotope effect on the direction of addition of perdeuterioborane to **15**) of 3-*endo*-3-*exo*-dideuterio-*exo*-2-norbornanol (**16**) and 2-*endo*-3-*exo*-dideuterio-*exo*-2-norbornanol (**17**).

Rearrangement of the α-chloro adduct **13** with inversion ultimately gives 2-*exo*-3-*exo*-dideuterio-2-*endo*-norbornanol (**18**), whereas rearrangement with retention will ultimately give **17**. In the deuterioboration of **12**, the alcohol **16** will provide the internal probe for analysis of the mechanistic path followed.

Experimentally, the deuterioboration of **12** gives, after basic oxidation, 59.6% **18**, 6.7% **16**, 6.7% **17**, and substantial quantities of norbornene (see the Experimental Section for the details of the analysis).

(12) The hydroboration of norbornene proceeds by >99% *exo* addition of borane [H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 2544 (1961)]. The introduction of the 2-chloro group should not affect the stereochemistry of attack by the perdeuterioborane.

(13) The stereochemistry of adduct **14** is not favorable for a facile *trans*-β-elimination. It appears that the *trans* elimination with **14** is much slower than with **7** leading to lower yields of subsequent deuterioboration products of **15**, and a greater yield of olefin **15** which is formed by a hydroxide-catalyzed elimination during the work-up. It appears that none of the adduct **14** survives the initial hydrolysis with aqueous sodium hydroxide prior to oxidation in that there is no chlorohydrin or epoxide (formed by the reaction of base on the chlorohydrin) detected in the final reaction product mixture by glpc techniques.

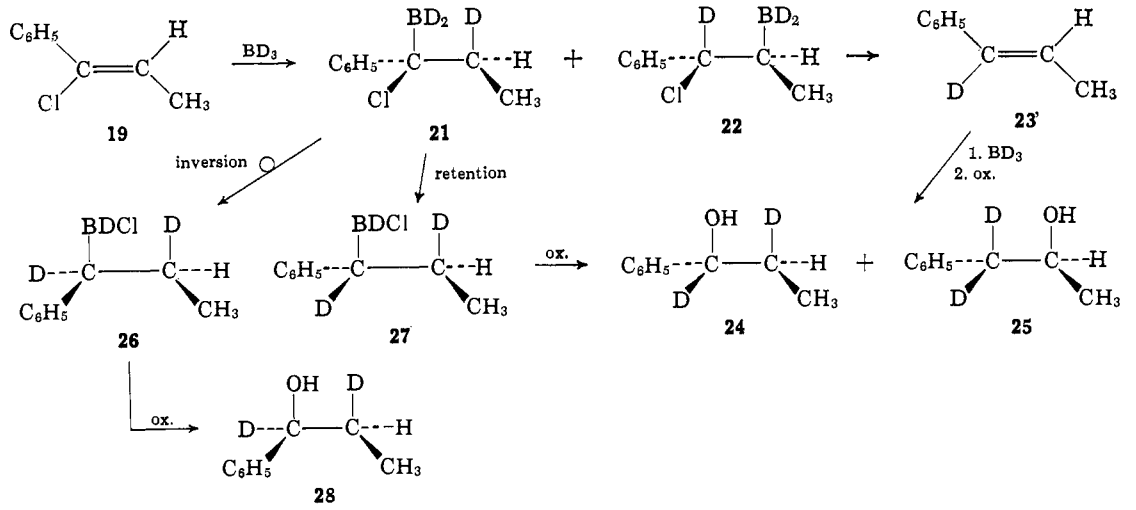
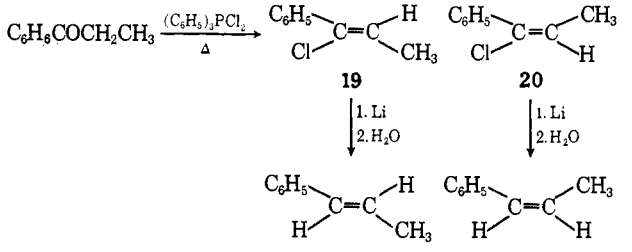


Figure 3. Products formed in the deuterioboration of 1-chloro-*trans*-1-phenylpropene (**19**).

Again, the rearrangement of the α-chloroorganoborane must be occurring with complete inversion.

The stereochemistry of the rearrangement in an acyclic system has also been determined utilizing 1-chloro-1-phenylpropene. Treatment of propiophenone with triphenylphosphine dichloride in refluxing benzene produces a mixture of 1-chloro-*cis*- and -*trans*-1-phenylpropene. The stereochemistry of the 1-chloro-1-phenylpropenes has been assigned previously solely on the basis of spectral evidence.[14] As the correct assignment of the stereochemistry of the rearrangement relies on knowing the stereochemistry of the 1-chloro-1-phenylpropenes with certainty, we felt it was necessary to obtain chemical evidence in support of the previous assignment of the stereochemistry of the two chloroolefins. Each of the chloroolefins was converted to the corresponding vinyllithium derivative and hydrolyzed to produce the propenylbenzenes. Employing this procedure, the chloroolefin previously assigned the *trans* stereochemistry produced predominantly *trans*-propenylbenzene (72%) and the previously assigned *cis*-chloroolefin produced predominantly *cis*-propenylbenzene (87%) in complete agreement with the prior assignments.[15] The more plentiful 1-chloro-*trans*-1-



phenylpropene was employed in the study of the stereochemistry of the rearrangement of an acyclic α-chloroorganoborane.

Deuterioboration of 1-chloro-*trans*-1-phenylpropene (**19**) will give the α-chloro adduct **21** and β-chloro adduct **22** (see Figure 3). The *trans* elimination involving **22** will give 1-deuterio-*trans*-1-phenylpropene (**23**) which on subsequent deuterioboration and basic oxidation will give *erythro*-1,2-dideuterio-1-phenyl-1-propanol (**24**) and 1,1-dideuterio-1-phenyl-2-propanol (**25**). Rearrangement of the α-chloro adduct **21** with inversion gives **26** which on subsequent oxidation gives *threo*-1,2-dideuterio-1-phenyl-1-propanol (**28**), whereas rearrangement with retention *via* **27** ultimately gives *erythro*-1,2-dideuterio-1-phenyl-1-propanol (**24**). As in the hydroboration of 2-methylchlorocyclohexene (**6**), the deuterioboration products of the intermediate olefin **23** may be employed as the internal probe for distinguishing the stereochemistry of the rearrangement: rearrangement with inversion giving rise to **28**, **24**, and **25** with the latter two appearing in a ratio of 6.7:1 (the ratio of **24** and **25** formed by direct deuterioboration of **23**); rearrangement with retention producing only **24** and **25** in a ratio of greater than 6.7:1; and rearrangement *via* a carbene complex giving **28**, **24**, and **25** with the latter two appearing in a ratio greater than 6.7:1.

The authentic *erythro*- and *threo*-1,2-dideuterio-1-phenyl-1-propanols, required for determination of the nmr spectral parameters of the corresponding benzoates for analysis of the product formed in the deuterioboration of **19** (see the Experimental Section for details), were prepared as outlined below. Deuteration of methylphenylacetylene over palladium on barium sulfate produced *cis*-1,2-dideuterio-1-phenylpropene (**29**). *trans*-1,2-Dideuterio-1-phenylpropene (**30**) was prepared by isomerization of **29** in the presence of iodine in refluxing hexane. The pure *cis* and *trans* olefins (purified by preparative glpc) were hydroborated producing the *erythro* and *threo* alcohols, respectively, in addition to lesser quantities of the diastereomeric 1,2-dideuterio-1-phenyl-2-propanols (**31** and **32**, respectively). Pure samples of **24** and **28** were obtained by preparative glpc.

Experimentally, the deuterioboration of 1-chloro-*trans*-1-phenylpropene (**19**) produced 3.8% 1-phenyl-2-propanol, 79% of 1-phenyl-1-propanol, <3% propiophenone, and <2% propylbenzene (by glpc). The 1-phenyl-1-propanol fraction was collected by preparative glpc, converted to the benzoate, and analyzed by nmr indicating the presence of 32.1% *erythro*- and 67.9% *threo*-1,2-dideuterio-1-phenyl-1-propanol. The formation of 3.8% 1-phenyl-2-propanol from **22**

(14) R. C. Fahey and C. S. Schubert, *J. Am. Chem. Soc.*, 87, 5172 (1965).

(15) After completion of these experiments the equilibration of the two chloroolefins over palladium on charcoal was reported [R. C. Fahey and D. J. Lee, *ibid.*, 88, 5555 (1966)], the previously assigned *cis*-chloroolefin undergoing isomerization to the *trans*-chloroolefin.

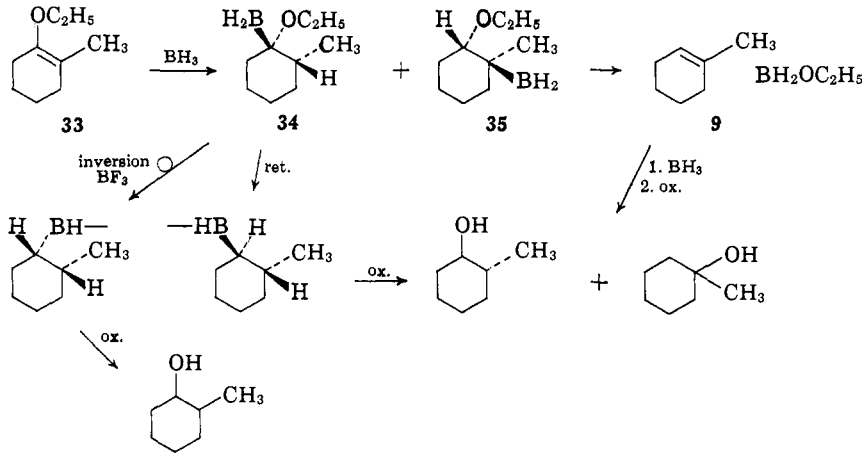
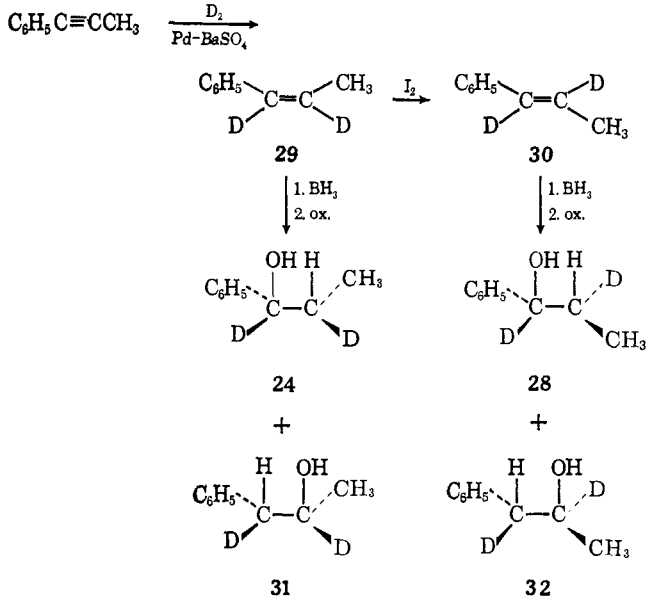


Figure 4. Products formed in the hydroboration of 1-ethoxy-2-methylcyclohexene (**33**) in the presence of boron trifluoride etherate.

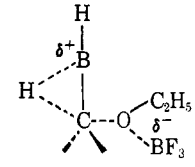
requires the simultaneous formation of 25.5% *erythro*-1,2-dideuterio-1-phenyl-1-propanol (**24**) thus accounting for all (25.3%) of **23**, within experimental limits of analysis, formed in the deuterioboration of **19**. Again, the rearrangement of the α-chloroorganoborane **21** occurs with complete inversion.



**Stereochemistry of the Acid-Catalyzed α-Transfer Reaction.** In our initial studies on the hydroboration of enol ethers,[4] it was observed that treatment of the intermediate β-ethoxyorganoborane, derived by hydroboration of β-ethoxystyrene, with boron trifluoride etherate produced acid-catalyzed transfer reactions as well as acid-catalyzed elimination reactions. Unfortunately, the hydroboration of enol ethers produces predominantly the β-alkoxyorganoborane (~90%) thus making it experimentally unfeasible to observe the α-transfer reaction. However, it was also observed that hydroboration of an enol ether in the presence of boron trifluoride results in a substantially greater amount of α-alkoxyorganoborane formation[4] (64% in the case of 4-*t*-butylethoxycyclohexene). Thus carrying out the hydroboration of an appropriately substituted enol ether in the presence of boron trifluoride will lead to the production of the required α-alkoxyorganoborane and will also provide the required Lewis acid to catalyze the α-transfer reaction.

2-Methylethoxycyclohexene (**33**) was selected as the substrate for determining the stereochemistry of the acid-catalyzed α-transfer reaction. Hydroboration of **33** in the presence of boron trifluoride will produce the α- and β-alkoxyorganoboranes **34** and **35** (see Figure 4). In the presence of boron trifluoride **35** will undergo elimination to give 1-methylcyclohexene which in turn on subsequent hydroboration will produce *trans*-2-methylcyclohexanol and 1-methylcyclohexanol. Acid-catalyzed rearrangement of **34** with inversion ultimately yields *cis*-2-methylcyclohexanol, whereas rearrangement with retention will ultimately give *trans*-2-methylcyclohexanol. Distinction of the stereochemistry of the rearrangement follows the same line of reasoning as outlined for **6**.

Experimentally, the hydroboration of 2-methylethoxycyclohexene (**33**) yields 6.5% *cis*-2-methylcyclohexanol, 27.1% *trans*-2-methylcyclohexanol, 2.4% 1-methylcyclohexanol, and 29.8% 1-methylcyclohexene. The results clearly indicate that the acid-catalyzed α transfer occurs with complete inversion and can be pictured as proceeding *via* the following transition state **36**.



In our earlier investigation on the hydroboration of enol ethers we also observed that the transfer reactions could be catalyzed by strong base (alkoxide).[4] We have not been successful in devising a system in which the stereochemistry of the base-catalyzed α transfer can be determined.

## Summary

In the present study we have shown that the rearrangement of α-chloroorganoboranes to alkylchloroboranes in cyclic and acyclic systems occurs with complete inversion. Although the present study employed chlorine as the heterofunctional group and ethoxyl in the acid-catalyzed rearrangement, we see no reason why

the stereochemistry of the α-transfer reactions involving other heterofunctional groups should differ.

We prefer to write the mechanism of the α-transfer reaction as involving an intramolecular rearrangement. An intermolecular nucleophilic displacement is theoretically possible; however, nucleophilic displacements are quite sensitive to the steric requirements for approach of the nucleophile. In the present cases, and in the case of alkyl transfer,[3] the nucleophilic attack must occur by delivery of hydride by another molecule of borane or alkylborane at a quaternary carbon atom and hence should not be a favorable reaction. In the intramolecular mechanism, the steric demands are much less. Further experiments are in progress to determine the molecularity of the reaction.[15a]

## Experimental Section

**Reagents.** The lithium aluminum deuteride used in these experiments was purchased from Metal Hydrides, Inc., Beverly, Mass. The borane-$d_3$ in tetrahydrofuran was prepared by the addition of boron trifluoride ethyl etherate to a suspension of lithium aluminum deuteride in diglyme, the liberated diborane-$d_6$ being transported in a stream of dry nitrogen and bubbled into a flask of cold tetrahydrofuran. The borane-$d_3$ tetrahydrofuran solutions were standardized by gas evolution measurements on hydrolysis with water.

**1-Chloro-2-methylcyclohexene (6).** The general procedure of Horner, Oediger, and Hoffmann[16] was employed. To a solution of 37.1 g (0.14 mole) of triphenylphosphine in 125 ml of dry benzene at 0° was added slowly 10.0 g (0.14 mole) of chlorine in 30 ml of carbon tetrachloride, keeping the temperature below 6°. The ice bath was removed, and 14.3 g (0.14 mole) of freshly distilled triethylamine in 10 ml of benzene and 15.9 g (0.14 mole) of 2-methylcyclohexanone in 10 ml of benzene were added. The reaction mixture was refluxed for 2 hr during which time the first precipitate ($Ph_3P \cdot Cl_2$) disappeared with the subsequent formation of triethylamine hydrochloride. The reaction mixture was cooled and the precipitate was removed by filtration. The filtrate was concentrated under reduced pressure. As the benzene was removed, triphenylphosphine oxide precipitated out and was removed by filtration. The triphenylphosphine oxide was washed several times with ether, and the ether washings were combined with the filtrate. The ether was removed by distillation, and the residue was distilled at 150–158°. The infrared spectrum of the distillate indicated the presence of some starting ketone. Column chromatography on Florisil with hexane as eluent gave a mixture of 1-chloro-2-methylcyclohexene and 1-chloro-6-methylcyclohexene which were separated by preparative glpc techniques on a 20-ft 20% Carbowax 20M on Chromosorb P column. The nmr of the desired chloroolefin was consistent with the assigned structure.

*Anal.* Calcd for $C_7H_{11}Cl$: C, 64.37; H, 8.49. Found: C, 64.82; H, 8.47.

***trans*-2-Methylcyclohexanol.** *trans*-2-Methylcyclohexanol was obtained from Professor E. L. Eliel.

***cis*-2-Methylcyclohexanol.** A mixture of 3 g (0.09 mole) of concentrated hydrochloric acid, 27 g (0.45 mole) of glacial acetic acid, 10.0 g (0.09 mole) of 2-methylcyclohexanone, and 2 g of platinum oxide was hydrogenated on a Parr hydrogenator, the theoretical amount of hydrogen being absorbed in 2 hr at an initial pressure of 46 psig. The reaction mixture was filtered, poured into ice–water, and extracted with ether. The combined ether extract was dried over anhydrous magnesium sulfate and concentrated to one-third its original volume by distillation.

The resulting ether solution was added to a solution of 10.0 g (0.25 mole) of sodium hydroxide and 200 ml of absolute ethanol and refluxed for 5 hr. The reaction mixture was hydrolyzed with water and extracted with ether; the combined ether extract was dried over anhydrous magnesium sulfate. The ether and ethanol were removed by distillation, and the product (72%) was distilled at 164–165°; $n^{20}D$ 1.4629 [lit.[17] bp 50.5° (2.9 mm), $n^{20}D$ 1.4649]. Analysis by glpc showed the presence of 17.8% *trans*-2-methylcyclohexanol and 82.2% *cis*-2-methylcyclohexanol. Pure *cis* alcohol was obtained by preparative glpc on a 30-ft 30% Carbowax 20M on Chromosorb W column.

**1-Methylcyclohexanol.** 1-Methylcyclohexanol was prepared by the procedure of Mosher.[18]

**1-Methylcyclohexene.** 1-Methylcyclohexene was prepared by the procedure of Bartlett and Rosenwald.[19]

**The Hydroboration of 1-Chloro-2-methylcyclohexene.** 1-Chloro-2-methylcyclohexene (**6**) (0.8 g, 6.2 mmoles) was dissolved in 25 ml of diglyme (distilled from lithium aluminum hydride) and treated with an excess of diborane, external generation from 5.62 g of boron trifluoride ethyl etherate and 1.50 g of sodium borohydride in 100 ml of dry diglyme, at 0° under an atmosphere of dry nitrogen. The reaction mixture was allowed to stand with stirring, under nitrogen for 5 hr.

An aliquot of 12.0 ml of the reaction mixture was removed, hydrolyzed with water, and oxidized with 1.0 ml of 20% sodium hydroxide solution and 0.5 ml of 30% hydrogen peroxide at 0°. The reaction mixture was extracted with ether, and the ether extract was dried over anhydrous magnesium sulfate. The ethereal solution was analyzed by glpc employing a 20-ft 20% Carbowax 20M on Firebrick column indicating the presence of 41.1% *cis*-2-methylcyclohexanol, 31.3% *trans*-2-methylcyclohexanol, 2.7% 1-methylcyclohexanol, and a trace of 1-methylcyclohexene.

To the remaining portion of the reaction mixture was added slowly 3.0 g (17.4 mmoles) of *m*-chloroperbenzoic acid[6] at 0°. The reaction mixture was kept under a nitrogen atmosphere. After 7 days, the reaction mixture was extracted with a 5% solution of ferrous ammonium sulfate acidified with a few drops of concentrated sulfuric acid. The diglyme layer was then washed with concentrated sodium bicarbonate and water and then dried over anhydrous magnesium sulfate. The products were analyzed as described above indicating the presence of 37.7% *cis*-2-methylcyclohexanol, 29.9% *trans*-2-methylcyclohexanol, 2.4% 1-methylcyclohexanol, and a trace of 1-methylcyclohexene.

**2-Chloronorbornene (12).** 2-Chloronorbornene was prepared by the procedure outlined in the preparation of 1-chloro-2-methylcyclohexene employing 22.5 g (0.2 mole) of norcamphor, 52.6 g (0.2 mole) of triphenylphosphine, 14.2 g (0.2 mole) of chlorine, and 20.3 g (0.2 mole) of triethylamine.

The reaction mixture was distilled under reduced pressure and the liquid boiling between 40 and 70° (46 mm) was collected. The infrared spectrum of the distillate indicated the presence of some starting ketone. Column chromatography on Florisil with hexane as eluent gave 2-chloronorbornene, bp 65.5° (44 mm), $n^{20}D$ 1.4889 [lit.[20] bp 50–55°(41 mm), $n^{25}D$ 1.4875].

***exo*-2-Norbornyl Acetate.** To a solution of 2.0 g (0.019 mole) of *exo*-norbornanol in 10 ml of pyridine at 0° was added 2 ml of acetyl chloride. The reaction mixture was allowed to stand at room temperature for 15 hr, then hydrolyzed with ice–water, and extracted with ether. The ether extracts were washed with saturated sodium bicarbonate solution, 10% sulfuric acid, and dried over anhydrous magnesium sulfate. The ether was removed under reduced pressure, and the product was distilled at 103° (40 mm), yield 100% [lit.[21] 89–90° (20 mm)]. The nmr spectrum in deuteriochloroform displayed the following peaks: −0.81 to −1.78 ppm (relative to tetramethylsilane) multiplet (8 H), −2.00 ppm singlet (3 H, $CH_3CO$), −2.26 ppm broad singlet (2 H, bridgehead hydrogens), and −4.54 ppm multiplet (1 H, >C*H*OAc).

***endo*-2-Norbornanol.** To a solution of 1.0 g (0.026 mole) of lithium aluminum hydride in 50 ml of dry ether was added 4.32 g (0.039 mole) of norcamphor. After stirring for 5 min, the reaction was quenched with 450 ml of 2 *N* sodium hydroxide solution. The water layer was extracted with ether; the ether extracts were washed

(15a) NOTE ADDED IN PROOF. Recent kinetic investigations in our laboratories have revealed that the α-transfer reaction is strictly intramolecular (first order in the α-substituted organoborane), and that the α-transfer reactions involving α-chloroorganoboranes are exceedingly sensitive to acid catalysis, both borane and boron trifluoride. Due to the exceedingly fast catalyzed reactions, the kinetic dependence on α-chloroorganoborane and Lewis acid cannot be determined. Except for the experiments with **33**, the possibility that the rearrangements of **7**, **13**, and **21** are acid catalyzed cannot be discounted. These reactions are very fast, and characterization of the intermediates **7**, **13**, and **21** by $B^{11}$ nmr has not been possible. As these reactions are catalyzed by boron trifluoride, as well as borane, we believe that the transfer of hydride from boron to carbon is intramolecular and occurs with inversion, and that the uncatalyzed reaction occurs *via* eq 5.

(16) L. Horner, H. Oediger, and H. Hoffmann, *Ann.*, **626**, 26 (1959).

(17) L. M. Jackman, A. K. MacBeth, and J. A. Mills, *J. Chem. Soc.*, 1717 (1949).

(18) W. A. Mosher, *J. Am. Chem. Soc.*, **62**, 552 (1940).

(19) P. D. Bartlett and R. H. Rosenwald, *ibid.*, **56**, 1990 (1934).

(20) J. D. Roberts, F. O. Johnson, and R. A. Carboni, *ibid.*, **76**, 5692 (1954).

(21) G. Komppa and S. Beckman, *Ann.*, **512**, 172 (1934).

with 2 *N* sulfuric acid and dried over potassium carbonate. The ether was removed under reduced pressure giving a white solid, which after two sublimations gave mp 148–149°, yield 82% (lit.[22] 149–150°).

*endo*-**2-Norbornyl Acetate.** *endo*-2-Norbornyl acetate was prepared by the procedure outlined in the preparation of *exo*-2-norbornyl acetate employing 0.8 g (7.8 mmoles) of *endo*-2-norbornanol. The desired acetate was obtained at bp 81–83° (12 mm), yield 100% [lit.[22] 81–83° (12 mm)]. The nmr spectrum displayed the following peaks: −0.96 to −1.69 ppm multiplet (8 H), −2.04 ppm singlet (3 H, $CH_3CO$), −2.18 ppm broad singlet (1 H, bridgehead hydrogen), −2.48 ppm broad singlet (1 H, bridgehead hydrogen), and −4.96 ppm double doublet (1 H, C*H*OAc).

**Deuterioboration of 2-Chlorononbornene.** To 4.0 ml of 1.62 *M* borane-$d_3$ in tetrahydrofuran solution at 0° was added slowly, under nitrogen, 0.5 g (3.9 mmoles) of 2-chlorononbornene (**12**) in 7.0 ml of dry tetrahydrofuran. The reaction mixture was stirred at 0° for 1 hr and then hydrolyzed with water and oxidized by the addition of 1.0 ml of 20% sodium hydroxide and 0.5 ml of 30% hydrogen peroxide, and worked up as described above. The ethereal solution was analyzed by glpc employing a 20-ft 20% Carbowax 20M on Firebrick column indicating the presence of 13.2% *exo*-norbornanol, 59.6% *endo*-norbornanol, 5.5% norcamphor, and 5.5% norbornene.

The ether was removed by distillation under reduced pressure leaving a white solid containing only the norbornanols and norcamphor. Norcamphor was removed from the norbornanols by employing the method of Fieser[23] (formation of the norcamphor trimethylaminoacetohydrazone chloride with Girard's T. reagent). The derivatized norcamphor was removed by extraction with water, the norbornanols remaining in the ether fraction. The ether was removed under reduced pressure. The norbornyl acetates were prepared as previously described and purified by distillation under reduced pressure. Analysis of the resulting mixture of acetates by nmr spectroscopy, utilizing the spectral parameters given in the foregoing experimental sections, indicated that **16** and **17** were present in equal amounts.

**1-Chloro-*trans*-1-phenylpropene (19).** 1-Chloro-*trans*-1-phenylpropene was prepared by the procedure outlined for the preparation of 1-chloro-2-methylcyclohexene employing 33.0 g (0.245 mole) of propiophenone, 92.7 g (0.353 mole) of triphenylphosphine, 20.5 g (0.373 mole) of chlorine, and 37.7 g (0.373 mole) of triethylamine.

The crude reaction mixture was distilled at reduced pressure, and the liquid boiling between 58 and 65° (0.6 mm) was collected. The infrared spectrum of the distillate indicated the presence of some starting ketone. Column chromatography on Florisil with elution with hexane gave a mixture of compounds, bp 44–47° (0.3 mm).

Glpc analysis indicated the presence of three compounds; 10% (A), 15% (B), and 75% (C). The mixture was separated by preparative glpc on a 20-ft 30% diethylene glycol succinate on Chromosorb P column. Fraction A was identified as methylphenylacetylene. Fractions B and C were tentatively identified as *cis*- and *trans*-1-chloro-1-phenylpropene, respectively, on the basis of their nmr spectra[14] and glpc retention times.

**Conversion of 1-Chloro-*cis*-1-phenylpropene to *cis*-Propenylbenzene.** To a solution of 0.05 g (0.33 mmole) of 1-chloro-*cis*-1-phenylpropene (**20**) in 5.0 ml of anhydrous ether at −35° was added 0.02 g (2.9 g-atoms) of freshly cut lithium wire. The reaction mixture was stirred at −35° for 4 hr and then hydrolyzed with 0.25 ml of water. The ether layer was decanted and the aqueous layer was extracted with ether. The combined ether extract was dried over anhydrous magnesium sulfate and analyzed by glpc on a 10-ft 20% diethylene glycol succinate on Chromosorb P column indicating the presence of *cis*-propenylbenzene (87%) and *trans*-propenylbenzene (13%).

**Conversion of 1-Chloro-*trans*-1-phenylpropene to *trans*-Propenylbenzene.** 1-Chloro-*trans*-1-phenylpropene (**19**) was treated with lithium at 0° as described for 1-chloro-*cis*-1-phenylpropene, and the products were analyzed by glpc indicating the presence of *cis*-propenylbenzene (28%) and *trans*-propenylbenzene (72%).

***cis*-1,2-Dideuterio-1-phenylpropene (29).** A mixture of a solution of 2.0 g (0.017 mole) of methylphenylacetylene in 55 ml of methanol containing four drops of quinoline was semideuterated over 0.1 g of 5% palladium on barium sulfate at atmospheric pressure. The catalyst was removed by filtration and the methanol was removed by distillation. Glpc analysis of the product indicated the presence of four compounds which were identified, in order of elution, as methylphenylacetylene (2%), 1,1,2,2-tetradeuterio-1-phenylpropane (23%), *cis*-1,2-dideuterio-1-phenylpropene (65%), and *trans*-1,2-dideuterio-1-phenylpropene (10%).

Fractions three and four were isolated by preparative glpc on a 20-ft 30% diethylene glycol succinate on Chromosorb P column.

The nmr spectrum of *cis*-1,2-dideuterio-1-phenylpropene displayed the following peaks: −1.74 ppm broadened singlet (3 H, $=CDCH_3$) and −7.16 ppm singlet (5 H, aromatic hydrogens).

**Isomerization of *cis*- to *trans*-1,2-Dideuterio-1-phenylpropene.** A solution of 7.5 g of the crude semideuteration mixture in 1 l. of hexane with four crystals of iodine was refluxed for 28 hr. The hexane solution was washed with aqueous sodium thiosulfate and dried over anhydrous magnesium sulfate, and the hexane was removed by distillation. The *trans*-1,2-dideuterio-1-phenylpropene was isolated by preparative glpc.

The nmr spectrum of *trans*-1,2-dideuterio-1-phenylpropene (**30**) displayed the following peaks: −1.69 ppm broadened singlet (3 H, $=CDCH_3$) and −7.15 ppm singlet (5 H, aromatic hydrogens).

***erythro*-1,2-Dideuterio-1-phenylpropanol (24).** To a solution of 9.60 ml (0.015 mole) of borane in tetrahydrofuran at 0° was added 1.5 g (0.013 mole) of *cis*-1,2-dideuterio-1-phenylpropene in 30 ml of tetrahydrofuran. The reaction mixture was stirred at 0° for 1.5 hr, after which 9.0 ml of 20% sodium hydroxide and 1.7 ml of 30% hydrogen peroxide were added slowly. The oxidized mixture was extracted with ether, and the combined ether extract was dried over anhydrous magnesium sulfate. The ether was removed by distillation under reduced pressure, and the remaining liquid was analyzed by glpc indicating the presence of two compounds with the same retention times as 1-phenyl-1-propanol (87%) and 1-phenyl-2-propanol (13%). The two fractions were isolated by preparative glpc on a 20-ft 20% Carbowax 20M on Chromosorb P column.

The nmr spectrum of *erythro*-1,2-dideuterio-1-phenyl-1-propanol displayed the following peaks: −0.75 ppm broadened doublet ($J$ = 7.4 Hz, 3 H, $-CHDCH_3$), −1.55 ppm broadened quartet ($J$ = 7.4 Hz, 1 H, $CHCDCH_3$), −4.66 ppm singlet (1 H, O*H*), and −7.15 ppm broadened singlet (5 H, aromatic hydrogens).

The nmr spectrum of *erythro*-1,2-dideuterio-1-phenyl-2-propanol (**31**) displayed the following peaks: −1.19 ppm broadened singlet (3 H, $CH_3$), −1.76 ppm singlet (1 H, −O*H*), −2.72 ppm broadened singlet (1 H, C*H*D), and −7.22 ppm broadened singlet (5 H, aromatic hydrogens).

***erythro*-1,2-Dideuterio-1-phenylpropyl Benzoate.** To a solution of 0.47 g (3.4 mmoles) of *erythro*-1,2-dideuterio-1-phenylpropanol in 3.0 ml of dry pyridine at 0° was added 0.51 g (3.6 mmoles) of freshly distilled benzoyl chloride. The reaction mixture was allowed to stand at room temperature for 7 days and then hydrolyzed with ice–water and extracted with ether. The combined ether extract was washed with 10% sodium bicarbonate, cold 10% sulfuric acid, and dried over anhydrous magnesium sulfate. The ether was removed by distillation under reduced pressure and the product (93%) was distilled in a microstill, approximate bp 82° (0.02 mm) [lit.[24] bp 190–192° (15 mm)]. The nmr spectrum of the product displayed the following peaks: −0.99 ppm broadened doublet ($J$ = 8.3 Hz, 3 H, $CH_3$), −1.90 ppm broadened quartet ($J$ = 8.3 Hz, 1 H, $CHDCH_3$), −7.32 and −8.07 ppm multiplets (10 H, aromatic hydrogens).

***threo*-1,2-Dideuterio-1-phenylpropanol (28).** *trans*-1,2-Dideuterio-1-phenylpropene was hydroborated as described for *cis*-1,2-dideuterio-1-phenylpropene, and the products were isolated by preparative glpc.

The nmr spectrum of *threo*-1,2-dideuterio-1-phenyl-1-propanol displayed the following peaks: −0.74 ppm broadened doublet ($J$ = 7.6 Hz, 3 H, $CH_3$), −1.62 ppm broadened quartet ($J$ = 7.6 Hz, 1 H, $CHDCH_3$), −4.63 ppm singlet (1 H, O*H*), and −7.15 ppm broad singlet (5 H, aromatic hydrogens).

The nmr spectrum of *threo*-1,2-dideuterio-1-phenyl-2-propanol (**32**) displayed the following peaks: −1.15 ppm broadened singlet (3 H, $CH_3$), −2.41 ppm singlet (1 H, O*H*), −2.63 ppm broadened singlet (1 H, C*H*D), and −7.19 ppm singlet (5 H, aromatic hydrogens).

(22) K. Alder and H. F. Rickert, *Ann.*, **543**, 1 (1939).

(23) L. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath and Co., Boston, Mass., p 88.

(24) L. Palfray, M. Mataijer, and J. Panouse, *Bull. Soc. Chim. France*, 766 (1947).

*threo*-**1,2-Dideuterio-1-phenylpropyl Benzoate.** *threo*-1,2-Dideuterio-1-phenylpropyl benzoate was prepared following the procedure outlined above for the *erythro* diastereoisomer.

The nmr spectrum displayed the following peaks: −0.93 ppm broadened doublet ($J$ = 7.5 Hz, 3 H, $CH_3$), −2.03 ppm broadened quartet ($J$ = 7.5 Hz, 1 H, $CHDCH_3$), and −7.37 and −8.08 ppm multiplets (10 H, aromatic hydrogens).

**Deuterioboration of 1-Chloro-*trans*-1-phenylpropene.** To 5.0 ml of 1.62 $M$ borane-$d_3$ in tetrahydrofuran solution at 0° was added slowly, under nitrogen, 1.00 g (6.55 mmoles) of 1-chloro-*trans*-1-phenylpropene (**19**) in 8.0 ml of dry tetrahydrofuran. The reaction was stirred at 0° for 5 days and then hydrolyzed with water and oxidized by the addition of 1.6 ml of 20% sodium hydroxide and 1.1 ml of 30% hydrogen peroxide and worked up as described above. The ethereal solution was analyzed by glpc employing a 20-ft 20% Carbowax 20M on Firebrick column indicating the presence of 79% 1-phenyl-1-propanol, 3.8% 1-phenyl-2-propanol, 3% propiophenone, and less than 2% *n*-propylbenzene.

The *erythro*- and *threo*-1,2-dideuterio-1-phenyl-1-propanols were isolated by preparative glpc and converted to the benzoates as described above.

The amounts of the *erythro* and *threo* diastereoisomers present were determined by nmr spectroscopy utilizing heteronuclear (deuterium) decoupling techniques. As the $CHDCH_3$ quartets in the nmr spectra of the two diastereoisomers overlap, lines 1 (low-field line) of the *erythro* isomer and 4 (high-field line) of the *threo* isomer were used to calculate the composition of the mixture. The relative intensities of these lines, with respect to the total quartet intensity in the two diastereoisomers, were determined by integration of the quartet lines in the spectra of the pure diastereoisomers. These values agreed within experimental error with the values calculated employing the Swalen–Reilly program.[25] This analytical approach indicated the presence of 32.1% *erythro*- and 67.9% *threo*-benzoates.

**1-Ethoxy-2-methylcyclohexene (33)** was prepared by the method of House and Kramar[26] and purified by preparative glpc on a 20-ft 20% Dow Corning silicone oil 550 on base-washed Diaport W column.

**1-Methyl-*trans*-2-ethoxy-1-cyclohexanol (38).** To a solution of 30.7 g (0.18 mole) of 85% *m*-chloroperbenzoic acid in 250 ml of dry methylene chloride was added 14.5 g (0.15 mole) of 1-methylcyclohexene at 0°. The temperature immediately rose to reflux temperature. The reaction was cooled and placed in the refrigerator for 14 hr. The *m*-chlorobenzoic acid was removed by washing with sodium bicarbonate. The organic layer was dried over anhydrous magnesium sulfate. The methylene chloride was removed by distillation and the product, 1-methyl-7-oxabicyclo-[4.1.0$^{1,6}$]heptane was distilled through a 2-ft, glass-helices-packed column giving a colorless liquid, bp 138–139°, $n^{20}$D 1.4426 (lit.[27] bp 138°, $n^{20}$D 1.4430).

To a solution of 13.8 g (0.06 g-atom) of sodium dissolved in 170 ml (2.91 moles) of absolute ethanol was added 3.0 g (0.027 mole) of 1-methyl-7-oxabicyclo[4.1.0$^{1,6}$]heptane. The reaction mixture was refluxed for 13 hr and then hydrolyzed with ice–water and extracted with ether. The ether extract was dried over anhydrous magnesium sulfate, and the ether was removed under reduced pressure. The product was distilled at 86.5–87.5° (14 mm).

*Anal.* Calcd for $C_9H_{18}O_2$: C, 68.31; H, 11.47. Found: C, 68.29; H, 11.80.

The nmr spectrum of the product in carbon tetrachloride displayed the following peaks: −1.12 ppm singlet (3 H, $CCH_3$), −1.18 ppm triplet ($J$ = 6.2 Hz, 3 H, $OCH_2CH_3$), −1.28 to −1.85 ppm multiplet (8 H, ring hydrogens), −2.95 ppm singlet (1 H, $OH$), −3.42 ppm quartet ($J$ = 6.2 Hz, 2 H, $OCH_2CH_3$), and −3.69 ppm multiplet (1 H, $CHOC_2H_5$).

***trans*-1-Ethoxy-2-methylcyclohexane.** To a solution of 3.3 g (0.029 mole) of *trans*-2-methylcyclohexanol and 3.9 g (0.049 mole) of pyridine at 0° was added 9.1 g (0.089 mole) of acetic anhydride. The reaction mixture was refluxed for 14 hr and then hydrolyzed with ice–water and extracted with ether. The ether extract was washed with saturated sodium bicarbonate and 10% hydrochloric acid, and dried over magnesium sulfate. The ether was removed by distillation under reduced pressure and the product, *trans*-2-methylcyclohexyl acetate (100%) was distilled at 62–63° (11 mm) [lit.[28] 63–64° (11.5 mm)].

*trans*-1-Ethoxy-2-methylcyclohexane was prepared by the procedure of Pettit and co-workers.[29] To a suspension of 8.8 g (0.23 mole) of lithium aluminum hydride in 150 ml of dry ether was added at 0° 110.0 g (0.78 mole) of boron trifluoride etherate and 4.5 g (0.029 mole) of *trans*-2-methylcyclohexyl acetate. The reaction mixture was refluxed for 1 hr and hydrolyzed cautiously by the addition of water. The aqueous layer was extracted with several portions of ether, and the combined ether extract was dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure, and the product (28%) was distilled in a microstill.

*Anal.* Calcd for $C_9H_{18}O$: C, 76.00; H, 12.76. Found: C, 76.06; H, 13.03.

***cis*-1-Ethoxy-2-methylcyclohexane.** *cis*-2-Methylcyclohexyl acetate was prepared from *cis*-2-methylcyclohexanol as described for *trans*-2-methylcyclohexyl acetate. The *cis*-2-methylcyclohexyl acetate was reduced following the procedure described for *trans*-2-methylcyclohexyl acetate giving a 33% yield of product which was distilled in a microstill.

*Anal.* Calcd for $C_9H_{18}O$: C, 76.00; H, 12.76. Found: C, 76.01; H, 12.70.

**Hydroboration of 1-Ethoxy-2-methylcyclohexene in the Presence of Boron Trifluoride Etherate.** To a solution of 0.21 g (1.53 mmoles) of 1-ethoxy-2-methylcyclohexene (**33**) and 0.19 g (1.53 mmoles) of boron trifluoride ethyl etherate in 3.0 ml of dry tetrahydrofuran at 0° was added slowly, under nitrogen, 1.50 ml of 1.02 $M$ borane in tetrahydrofuran solution. The reaction mixture was stirred for 1 hr at 0° and then hydrolyzed with water and oxidized by the addition of 0.5 ml of 20% sodium hydroxide and 0.25 ml of 30% hydrogen peroxide and worked up as described above. The ethereal solution was analyzed by glpc using a 20-ft 20% Carbowax 20M on Firebrick column and a 20-ft 20% 1,2,3-tris-(2-cyanoethoxy)propane on Firebrick column (not all products could be determined on a single column) indicating the presence of 6.5% *cis*-2-methylcyclohexanol, 27.1% *trans*-2-methylcyclohexanol, 1.3% *cis*-1-ethoxy-2-methylcyclohexane, 2.4% *trans*-1-ethoxy-2-methylcyclohexane, 10.5% 1-methyl-*trans*-2-ethoxy-1-cyclohexanol, 2.4% 1-methylcyclohexanol, 29.8% 1-methylcyclohexene, and 6.9% 2-methylcyclohexanone.

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